

## 5.0 Contaminant Geochemistry and $K_d$ Values

The important geochemical factors affecting the sorption<sup>1</sup> of cadmium (Cd), cesium (Cs), chromium (Cr), lead (Pb), plutonium (Pu), radon (Rn), strontium (Sr), thorium (Th), tritium (<sup>3</sup>H), and uranium (U) are discussed in this chapter. The objectives of this chapter are to: (1) provide a “thumb-nail sketch” of the key geochemical processes affecting sorption of these contaminants, (2) provide references to key experimental and review articles for further reading, (3) identify the important aqueous- and solid-phase parameters controlling contaminant sorption in the subsurface environment, and (4) identify, when possible, minimum and maximum conservative  $K_d$  values for each contaminant as a function key geochemical processes affecting their sorption.

### 5.1 General

Important chemical speciation, (co)precipitation/dissolution, and adsorption/desorption processes of each contaminant are discussed. Emphasis of these discussions is directed at describing the general geochemistry that occurs in oxic environments containing low concentrations of organic carbon located far from a point source (*i.e.*, in the far field). These environmental conditions comprise a large portion of the contaminated sites of concern to the EPA, DOE, and/or NRC. We found it necessary to focus on the far-field, as opposed to near-field, geochemical processes for 2 main reasons. First, the near field frequently contains very high concentrations of salts, acids, bases, and/or contaminants which often require unusual chemical or geochemical considerations that are quite different from those in the far field. Secondly, the differences in chemistry among various near-field environments varies greatly, further compromising the value of a generalized discussion. Some qualitative discussion of the effect of high salt conditions and anoxic conditions are presented for contaminants whose sorption behavior is profoundly affected by these conditions.

The distribution of aqueous species for each contaminant was calculated for an oxidizing environment containing the water composition listed in Table 5.1 and the chemical equilibria code MINTEQA2 (Version 3.10, Allison *et al.*, 1991). The water composition in Table 5.1 is based on a “mean composition of river water of the world” estimated by Hem (1985). We use this chemical composition simply as a convenience as a proxy for the composition of a shallow groundwater. Obviously, there are significant differences between surface waters and groundwaters, and considerable variability in the concentrations of various constituents in surface and groundwaters. For example, the concentrations of

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<sup>1</sup> When a contaminant is associated with a solid phase, it is commonly not known if the contaminant is adsorbed onto the surface of the solid, absorbed into the structure of the solid, precipitated as a 3-dimensional molecular coating on the surface of the solid, or absorbed into organic matter. “Sorption” will be used in this report as a generic term devoid of mechanism to describe the partitioning of aqueous phase constituents to a solid phase. Sorption is frequently quantified by the partition (or distribution) coefficient,  $K_d$ .

dissolved gases and complexing ligands, such as carbonate, may be less in a groundwater as a result of infiltration of surface water through the soil column. Additionally, the redox potential of groundwaters, especially deep groundwaters, will likely be more reducing than surface water. As explained later in this chapter, the adsorption and solubility of certain contaminants and radionuclides may be significantly different under reducing groundwater conditions compared to oxidizing conditions. However, it was necessary to limit the scope of this review to oxidizing conditions. Use of the water composition in Table 5.1 does not invalidate the aqueous speciation calculations discussed later in this chapter relative to the behavior of the selected contaminants in oxidizing and transitional groundwater systems. The calculations demonstrate what complexes might exist for a given contaminant in any oxidizing water as a function of pH and the specified concentrations of each inorganic ligand. If the concentration of a complexing ligand, such as phosphate, is less for a site-specific groundwater compared to that used for our calculations, then aqueous complexes containing that contaminant and ligand may be less important for that water.

Importantly, water composition in Table 5.1 has a low ionic strength and contains no natural (*e.g.*, humic or fulvic acids<sup>1</sup>) or anthropogenic (*e.g.*, EDTA) organic materials. The species distributions of thorium and uranium were also modeled using pure water, free of any ligands other than hydroxyl ions, to show the effects of hydrolysis in the absence of other complexation reactions. The concentrations used for the dissolved contaminants in the species distribution calculations are presented in Table 5.2 and are further discussed in the following sections. The species distributions of cesium, radon, and tritium were not determined because only 1 aqueous species is likely to exist under the environmental conditions under consideration; namely, cesium would exist as  $\text{Cs}^+$ , radon as  $\text{Rn}^0(\text{gas})$ , and tritium as tritiated water, HTO (T = tritium,  $^3\text{H}$ ).

Throughout this chapter, particular attention will be directed at identifying the important aqueous- and solid-phase parameters controlling retardation<sup>2</sup> of contaminants by sorption in soil. This information was used to guide the review and discussion of published  $K_d$  values according to the important chemical, physical, and mineralogical characteristics or variables. Perhaps more importantly, the variables had include parameters that were readily available to modelers. For instance, particle size and pH are often available to modelers whereas such parameters as iron oxide or surface area are not as frequently available.

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<sup>1</sup> “Humic and fulvic acids are breakdown products of cellulose from vascular plants. Humic acids are defined as the alkaline-soluble portion of the organic material (humus) which precipitates from solution at low pH and are generally of high molecular weight. Fulvic acids are the alkaline-soluble portion which remains in solution at low pH and is of lower molecular weight” (Gascoyne, 1982).

<sup>2</sup> Retarded or attenuated (*i.e.*, nonconservative) transport means that the contaminant moves slower than water through geologic material. Nonretarded or nonattenuated (*i.e.*, conservative) transport means that the contaminant moves at the same rate as water.

**Table 5.1.** Estimated mean composition of river water of the world from Hem (1985).<sup>1</sup>

| Dissolved Constituent  | Total Concentration |                       |
|--|---------------------|-----------------------|
|  | mg/l                | mol/l                 |
| Silica, as $\text{H}_4\text{SiO}_4$  | 20.8                | $2.16 \times 10^{-4}$ |
| Ca   | 15                  | $3.7 \times 10^{-4}$  |
| Mg   | 4.1                 | $1.7 \times 10^{-4}$  |
| Na   | 6.3                 | $2.7 \times 10^{-4}$  |
| K  | 2.3                 | $5.9 \times 10^{-5}$  |
| Inorganic Carbon, as $\text{CO}_3$   | 57                  | $9.5 \times 10^{-4}$  |
| $\text{SO}_4$  | 11                  | $1.1 \times 10^{-4}$  |
| Cl   | 7.8                 | $2.2 \times 10^{-4}$  |
| F  | 1                   | $5 \times 10^{-5}$    |
| $\text{NO}_3$  | 1                   | $2 \times 10^{-5}$    |
| $\text{PO}_4$  | 0.0767              | $8.08 \times 10^{-7}$ |
| <sup>1</sup> Most values from this table were taken from Hem (1985: Table 3, Column 3). Mean concentrations of total dissolved fluoride and phosphate are not listed in Hem (1985, Table 3). The concentration of dissolved fluoride was taken from Hem (1985, p. 120) who states that the concentration of total dissolved fluoride is generally less than 1.0 mg/l for most natural waters. Hem (1985, p. 128) lists 25 micro g/l for average concentration of total dissolved phosphorous in river water estimated by Meybeck (1982). This concentration of total phosphorus was converted to total phosphate ( $\text{PO}_4$ ) listed above. |                     |                       |

**Table 5.2.** Concentrations of contaminants used in the aqueous species distribution calculations.

| Element      | Total Conc.<br>(micro g/l) | Reference for Concentration of Contaminant<br>Used in Aqueous Speciation Calculations   |
|--------------|----------------------------|---|
| Cd           | 1.0                        | Hem (1985, p. 142) lists this value as a median concentration of dissolved cadmium based on the reconnaissance study of Duram <i>et al.</i> (1971) of metal concentrations in surface waters in the United States.  |
| Cs           | --                         | Distribution of aqueous species was not modeled, because mobility of dissolved cesium is not significantly affected by complexation (see Section 5.3).  |
| Cr           | 1.4                        | Hem (1985, p. 138) lists this value as an average concentration estimated by Kharkar <i>et al.</i> (1968) for chromium in river waters.   |
| Pb           | 1.0                        | Hem (1985, p. 144) lists this value as an average concentration estimated by Duram <i>et al.</i> (1971) for lead in surface-water samples from north- and southeastern sections of the United States.   |
| Pu           | $3.2 \times 10^{-7}$       | This concentration is based on the maximum activity of $^{239,240}\text{Pu}$ measured by Simpson <i>et al.</i> (1984) in 33 water samples taken from the highly alkaline Mono Lake in California.   |
| Rn           | --                         | Aqueous speciation was not calculated, because radon migrates as a dissolved gas and is not affected by complexation (see Section 5.7).   |
| Sr           | 110                        | Hem (1985, p. 135) lists this value as the median concentration of strontium for larger United States public water supplies based on analyses reported by Skougstad and Horr (1963).  |
| Th           | 1.0                        | Hem (1985, p. 150) gives 0.01 to 1 micro g/l as the range expected for thorium concentrations in fresh waters.  |
| $^3\text{H}$ | --                         | Aqueous speciation was not calculated, because tritium ( $^3\text{H}$ ) migrates as tritiated water.  |
| U            | 0.1 and<br>1,000           | Because dissolved hexavalent uranium can exist as polynuclear hydroxyl complexes, the hydrolysis of uranium under oxic conditions is therefore dependent on the concentration of total dissolved uranium. To demonstrate this aspect of uranium chemistry, 2 concentrations (0.1 and 1,000 micro g/l) of total dissolved uranium were used to model the species distributions. Hem (1985, p. 148) gives 0.1 to 10 microg/l as the range for dissolved uranium in most natural waters. For waters associated with uranium ore deposits, Hem states that the uranium concentrations may be greater than 1,000 microg/l. |

## 5.2 Cadmium Geochemistry and $K_d$ Values

### 5.2.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

The dominant cadmium aqueous species in groundwater at pH values less than 8.2 and containing moderate to low concentrations of sulfate ( $<10^{-2.5}$  M  $\text{SO}_4^{2-}$ ) is the uncomplexed  $\text{Cd}^{2+}$  species. The dominant cadmium solution species in groundwater at pH values greater than 8.2 are  $\text{CdCO}_3^0$  (aq) and to a smaller extent  $\text{CdCl}^+$ . Both precipitation/coprecipitation/dissolution and adsorption/desorption reactions control cadmium concentrations. Several researchers report that otavite ( $\text{CdCO}_3$ ) limits cadmium solution concentrations in alkaline soils. The solid  $\text{Cd}_3(\text{PO}_4)_2$  has also been reported to be a solubility-controlling solid for dissolved cadmium. Under low redox conditions, sulfide concentrations and the formation of Cd precipitates may play an important role in controlling the concentrations of dissolved cadmium. At high concentrations of dissolved cadmium ( $>10^{-7}$  M Cd), either cation exchange or (co)precipitation are likely to control dissolved cadmium concentrations. Precipitation with carbonate is increasingly important in systems with a pH greater than 8, and cation exchange is more important in lower pH systems. At lower environmental concentrations of dissolved cadmium, surface complexation with calcite and aluminum- and iron-oxide minerals may be the primary process influencing retardation. Transition metals (*e.g.*, copper, lead, zinc) and alkaline earth (*e.g.*, calcium, magnesium) cations reduce cadmium adsorption by competition for available specific adsorption and cation exchange sites. In conclusion, the key aqueous- and solid-phase parameters influencing cadmium adsorption include pH, cadmium concentration, competing cation concentrations, redox, cation exchange capacity (CEC), and mineral oxide concentrations.

### 5.2.2 General Geochemistry

Cadmium (Cd) exists in the +2 oxidation state in nature. It forms a number of aqueous complexes, especially with dissolved carbonate. Its concentration may be controlled by either adsorption or precipitation/coprecipitation processes. The extent to which cadmium is associated with or bound to soils varies greatly with type of mineral, oxidation state of the system, and presence of competing cations in solution.

Cadmium concentrations in uncontaminated soils is typically less than 1 mg/kg. However, concentrations may be significantly elevated by some human activities or by the weathering of parent materials with high cadmium concentrations, *e.g.*, black shales (Jackson and Alloway, 1992). Approximately 90 percent of all the cadmium consumed goes into 4 use categories: plating (35 percent), pigments (25 percent), plastic stabilizers (15 percent), and batteries (15 percent) (Nriagu, 1980b). Cadmium may also be introduced into the environment by land applications of sewage sludge. Cadmium concentrations in sewage sludge are commonly the limiting factor controlling land disposal (Juste and Mench, 1992). Nriagu (1980a) has edited an excellent review on the geochemistry and toxicity of cadmium.



### 5.2.3 Aqueous Speciation

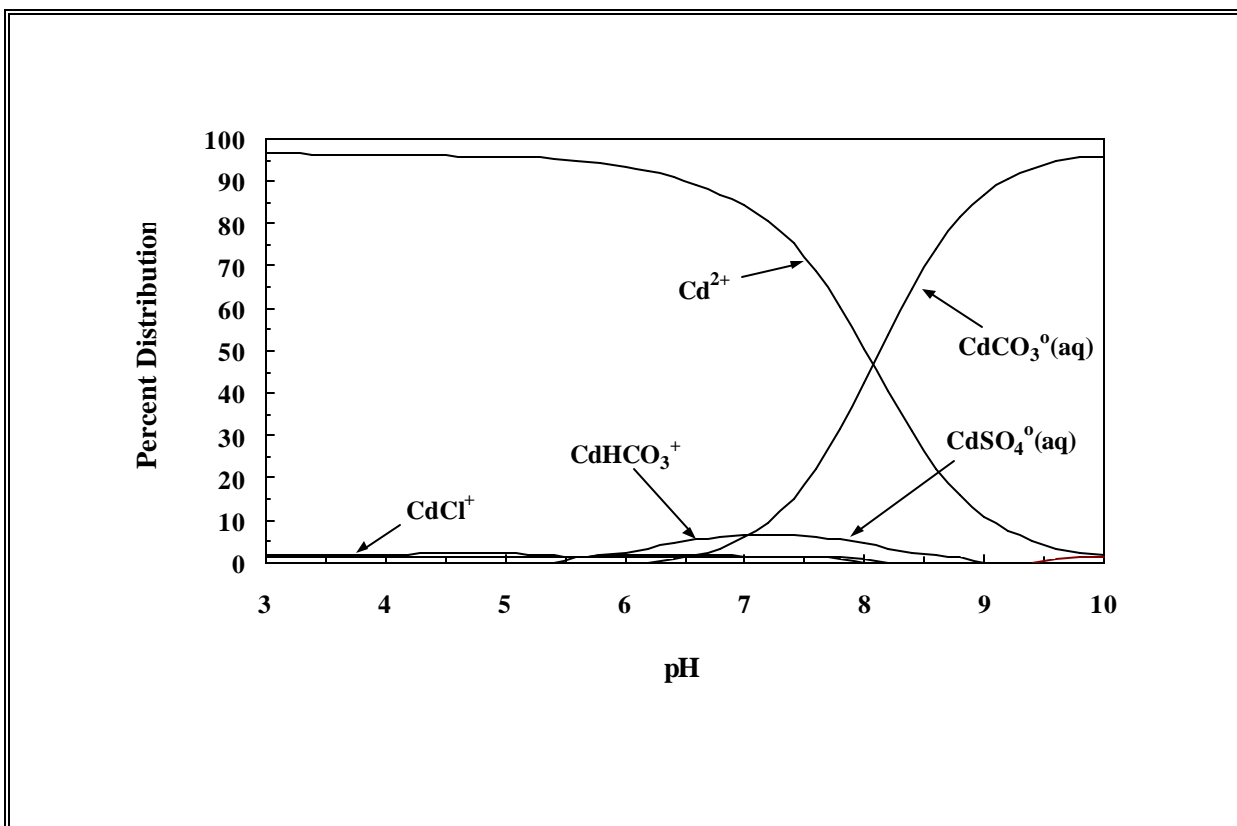
Cadmium forms soluble complexes with inorganic and organic ligands resulting in an increase of cadmium mobility in soils (McLean and Bledsoe, 1992). The distribution of cadmium aqueous species was calculated using the water composition described in Table 5.1 and a concentration of 1 micro g/l total dissolved cadmium (Table 5.2). Hem (1985, p. 142) lists this value as a median concentration of dissolved cadmium based on the reconnaissance study of Duram *et al.* (1971) of metal concentrations in surface waters in the United States. These MINTEQA2 calculations indicate that cadmium speciation is relatively simple. In groundwaters of pH values less than 6, essentially all of the dissolved cadmium is expected to exist as the uncomplexed  $\text{Cd}^{2+}$  ion (Figure 5.1). The aqueous species included in the MINTEQA2 calculations are listed in Table 5.3. As the pH increases between 6 and 8.2, cadmium carbonate species [ $\text{CdHCO}_3^+$  and  $\text{CdCO}_3^0$  (aq)] become increasingly important. At pH values between 8.2 and 10, essentially all of the cadmium in solution is expected to exist as the neutral complex  $\text{CdCO}_3^0$  (aq). The species  $\text{CdSO}_4^0$  (aq),  $\text{CdHCO}_3^+$ ,  $\text{CdCl}^+$ , and  $\text{CdOH}^+$  are also present, but at much lower concentrations. The species distribution illustrated in Figure 5.1 does not change if the concentration of total dissolved cadmium is increased from 1 to 1,000 micro g/l.

**Table 5.3.** Cadmium aqueous species included in the speciation calculations.

| Aqueous Species   |
|---|
| $\text{Cd}^{2+}$  |
| $\text{CdOH}^+$ , $\text{Cd}(\text{OH})_2^0$ (aq), $\text{Cd}(\text{OH})_3^-$ , $\text{Cd}(\text{OH})_4^{2-}$ , $\text{Cd}_2\text{OH}^{3+}$ |
| $\text{CdHCO}_3^+$ , $\text{CdCO}_3^0$ (aq), $\text{Cd}(\text{CO}_3)_3^{4-}$  |
| $\text{CdSO}_4^0$ (aq), $\text{Cd}(\text{SO}_4)_2^{2-}$   |
| $\text{CdNO}_3^+$   |
| $\text{CdCl}^+$ , $\text{CdCl}_2^0$ (aq), $\text{CdCl}_3^-$ , $\text{CdOHCl}^0$ (aq)  |
| $\text{CdF}^+$ , $\text{CdF}_2^0$ (aq)  |







**Figure 5.1.** Calculated distribution of cadmium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved cadmium and thermodynamic data supplied with the MINTEQA2 geochemical code.]

Information available in the literature regarding interactions between dissolved cadmium and naturally occurring organic ligands (humic and fulvic acids) is ambiguous. Weber and Posselt (1974) reported that cadmium can form stable complexes with naturally occurring organics, whereas Hem (1972) stated that the amount of cadmium occurring in organic complexes is generally small and that these complexes are relatively weak. Pittwell (1974) reported that cadmium is complexed by organic carbon under all pH conditions encountered in normal natural waters. Levi-Minzi *et al.* (1976) found cadmium adsorption in soils to be correlated with soil organic matter content. In a critical review of the literature, Giesy (1980) concluded that the complexation constants of cadmium to naturally occurring organic matter are weak because of competition for binding sites by calcium, which is generally present in much higher concentrations.

#### 5.2.4 Dissolution/Precipitation/Coprecipitation

Lindsay (1979) calculated the relative stability of cadmium compounds. His calculations show that at pH values less than 7.5, most cadmium minerals are more soluble than cadmium concentrations found in oxic soils ( $10^{-7}$  M), indicating that cadmium at these concentrations is not likely to precipitate. At pH levels greater than 7.5, the solubilities of  $\text{Cd}_3(\text{PO}_4)_2$  or  $\text{CdCO}_3$  may control the concentrations of cadmium in soils. Cavallaro and McBride (1978) and McBride (1980) demonstrated that otavite,  $\text{CdCO}_3$ , precipitates in calcareous soils ( $\text{pH} > 7.8$ ), whereas in neutral or acidic soils, adsorption is the predominate process for removal of cadmium from solution. Jenne *et al.* (1980), working with the waters associated with abandoned lead and zinc mines and tailings piles, also indicate that the upper limits on dissolved levels of cadmium in most waters were controlled by  $\text{CdCO}_3$ . Santillan-Medrano and Jurinak (1975) observed that the activity of dissolved cadmium in cadmium-amended soils was lowest in calcareous soils. Baes and Mesmer (1976) suggested that cadmium may coprecipitate with calcium to form carbonate solid solutions,  $(\text{Ca,Cd})\text{CO}_3$ . This may be an important mechanism in controlling cadmium concentrations in calcareous soils.

Although cadmium itself is not sensitive to oxidation/reduction conditions, its concentration in the dissolved phase is generally very sensitive to redox state. There are numerous studies (reviewed by Khalid, 1980) showing that the concentrations of dissolved cadmium greatly increase when reduced systems are oxidized, such as when dredged river sediments are land filled or rice paddies are drained. The following 2 mechanisms appear to be responsible for this increase in dissolved cadmium concentrations: (1) very insoluble CDs (greenockite) dissolves as sulfide  $[\text{S(II)}]$  that is oxidized to sulfate  $[\text{S(VI)}]$ , and (2) organic materials binding cadmium are decomposed through oxidization, releasing cadmium into the environment (Gambrell *et al.*, 1977; Giesy, 1980). This latter mechanism appears to be important only in environments in which moderate to high organic matter concentrations are present (Gambrell *et al.*, 1977). Serne (1977) studied the effect of oxidized and reduced sediment conditions on the release of cadmium from dredged sediments collected from the San Francisco Bay. Greater than 90 percent of the cadmium in the reduced sediment [sediment incubated in the presence of low  $\text{O}_2$  levels ( $\text{Eh} < 100$  mV)] was complexed with insoluble organic matter or precipitated as sulfides. The remainder of the cadmium was associated with the oxide minerals, clay lattices, or exchangeable sites. Dissolved cadmium concentrations greatly increased when the sediments were incubated under oxidizing conditions ( $\text{Eh} > 350$  mV). Cadmium concentrations released in the elutriate increased with agitation time. These data suggested that this kinetic effect was due to slow oxidation of sulfide or cadmium bound to organic matter bound in the reduced sediment prior to steady state equilibrium conditions being reached. In a similar type of experiment in which Mississippi sediments were slowly oxidized, Gambrell *et al.* (1977) reported that the insoluble organic- and sulfide-bound cadmium fractions in sediment decreased dramatically (decreased  $> 90$  percent) while the exchangeable and water-soluble cadmium fractions increased. Apparently, once the cadmium was released from the sulfide and organic matter fractions, the cadmium entered the aqueous phase and then re-adsorbed onto other sediment phases.

A third mechanism involves pyrite that may be present in soils or sediments and gets oxidized when exposed to air.<sup>1</sup> The pyrite oxidizes to form  $\text{FeSO}_4$ , which generates high amounts of acidity when reacted with water. The decrease in the pH results in the dissolution of cadmium minerals and increase in the dissolved concentration of cadmium. This process is consistent with the study by Kargbo (1993) of acid sulfate clays used as waste covers.

### 5.2.5 Sorption/Desorption

At high solution concentrations of cadmium ( $>10$  mg/l), the adsorption of cadmium often correlates with the CEC of the soil (John, 1971; Levi-Minzi *et al.*, 1976; McBride *et al.*, 1981; Navrot *et al.*, 1978; Petruzelli *et al.*, 1978). During cation exchange, cadmium generally exchanges with adsorbed calcium and magnesium (McBride *et al.*, 1982). The ionic radius of  $\text{Cd}^{2+}$  is comparable to that of  $\text{Ca}^{2+}$  and, to a lesser extent,  $\text{Mg}^{2+}$ . At low solution concentrations of cadmium, surface complexation to calcite (McBride, 1980) and hydrous oxides of aluminum and iron (Benjamin and Leckie, 1981) may be the most important adsorption mechanism. Both  $\text{Cd}^{2+}$  and possibly  $\text{CdOH}^+$  may adsorb to aluminum- and iron-oxide minerals (Balistrieri and Murray, 1981; Davis and Leckie, 1978).

As with other cationic metals, cadmium adsorption exhibits pH dependency. The effect of pH on cadmium adsorption by soils (Huang *et al.*, 1977), sediment (Reid and McDuffie, 1981), and iron oxides (Balistrieri and Murray, 1982; Levy and Francis, 1976) is influenced by the solution concentration of cadmium and the presence of competing cations or complexing ligands. At low cadmium solution concentrations, sharp adsorption edges (the range of pH where solute adsorption goes from  $\sim 0$  to  $\sim 100$  percent) suggests that specific adsorption (*i.e.*, surface complexation via a strong bond to the mineral surface) occurs. Under comparable experimental conditions, the adsorption edge falls at pH values higher than those for lead, chromium, and zinc. Thus, in lower pH environments, these metals, based on their propensity to adsorb, would rank as follows:  $\text{Pb} > \text{Cr} > \text{Zn} > \text{Cd}$ . This order is inversely related to the pH at which hydrolysis of these metals occurs (Benjamin and Leckie, 1981).

Competition between cations for adsorption sites strongly influences the adsorption behavior of cadmium. The presence of calcium, magnesium, and trace metal cations reduce cadmium adsorption by soils (Cavallaro and McBride, 1978; Singh, 1979), iron oxides (Balistrieri and Murray, 1982), manganese oxides (Gadde and Laitinen, 1974), and aluminum oxides (Benjamin and Leckie, 1980). The extent of competition between cadmium and other ions depends on the relative energies of interaction between the ions and the adsorbing surface, the concentrations of the competing ions, and solution pH (Benjamin and Leckie, 1981; Sposito, 1984). The addition of copper or lead, which are more strongly adsorbed, slightly reduces cadmium adsorption by iron and aluminum oxides, suggesting that copper and lead are preferentially adsorbed by different surface sites (Benjamin and Leckie,

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<sup>1</sup> D. M. Kargbo (1998, personal communication).

1980). In contrast, zinc almost completely displaces cadmium, indicating that cadmium and zinc compete for the same group of binding sites (Benjamin and Leckie, 1981).

Although organic matter may influence adsorption of cadmium by soils (John, 1971; Levi-Minzi *et al.*, 1976), this effect is probably due to the CEC of the organic material rather than to complexation by organic ligands (Singh and Sekhon, 1977). In fact, removal of organic material from soils does not markedly reduce cadmium adsorption and may enhance adsorption (Petruselli *et al.*, 1978). Clay minerals with adsorbed humic acids (organo-clay complexes) do not adsorb cadmium in excess of that expected for clay minerals alone (Levy and Francis, 1976).

### **5.2.6 Partition Coefficient, $K_d$ , Values**

#### **5.2.6.1 General Availability of $K_d$ Data**

A total of 174 cadmium  $K_d$  values were found in the literature and included in the data base used to create the look-up tables.<sup>1</sup> The cadmium  $K_d$  values as well as the ancillary experimental data are presented in Appendix C. Data included in this table were from studies that reported  $K_d$  values (not percent adsorption or Langmuir constants) and were conducted in systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (< 0.1 M), pH values between 4 and 10, low humic material concentrations (<5 mg/l), and no organic chelates (*e.g.*, EDTA). At the start of the literature search, attempts were made to identify cadmium  $K_d$  studies that reported ancillary data on aluminum/iron-oxide concentrations, calcium and magnesium solution concentrations, CEC, clay content,<sup>2</sup> pH, redox status, organic matter concentrations and sulfide concentrations. Upon reviewing the data and determining the availability of cadmium  $K_d$  studies reporting ancillary data, we selected data on clay content, pH, CEC, and total organic carbon. The selection of these parameters was based on availability of data and the possibility that the parameter may impact cadmium  $K_d$  values. Of the 174 cadmium  $K_d$  values included in the compiled data, only 62 values had associated clay content data, 174 values had associated pH data, 22 values had associated CEC data, 63 values had total organic carbon data, and 16 had associated aluminum/iron-oxide data. Descriptive statistics and a correlation coefficient matrix are presented in Appendix C.

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<sup>1</sup> Since the completion of our review and analysis of  $K_d$  data for the selected contaminants and radionuclides, the study by Wang *et al.* (1998) was identified and may be of interest to the reader.

<sup>2</sup> Unless specified otherwise, “clay content” refers to the particle size fraction of soil that is less than 2 micro m.

#### 5.2.6.2 Look-Up Tables

One cadmium  $K_d$  look-up table was created. The table requires knowledge of the pH of the system (Table 5.4). The pH was selected as the key independent variable because it had a highly significant ( $P < 0.001$ ) correlation with cadmium  $K_d$ , a correlation coefficient value of 0.75. A detailed explanation of the approach used in selecting the  $K_d$  values used in the table is presented in Appendix C. Briefly, it involved conducting a regression analysis between pH and  $K_d$  values). The subsequent regression equation was used to provide central estimates. Minimum and maximum values were estimated by plotting the data and estimating where the limits of the data existed.

There is an unusually wide range of possible cadmium  $K_d$  values for each of the 3 pH categories. The cause for this is likely that there are several other soil parameters influencing the  $K_d$  in addition to pH. Unfortunately, the correlations between the cadmium  $K_d$  values and the other soil parameters in this data set were not significant (Appendix C).

##### 5.2.6.2.1 Limits of $K_d$ Values With Respect to Aluminum/Iron-Oxide Concentrations

The effect of iron-oxide concentrations on cadmium  $K_d$  values was evaluated using the data presented in Appendix C. Of the 174 cadmium  $K_d$  values in the data set presented in Appendix C, only 16 values had associated iron oxide concentration data. In each case iron, and not aluminum, oxide concentration data were measured. The correlation coefficient describing the linear relationship between cadmium  $K_d$  values and iron oxide concentration was 0.18, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between iron or aluminum oxide concentrations and cadmium  $K_d$  values because oxide minerals provide adsorption (surface complexation) sites.

**Table 5.4.** Estimated range of  $K_d$  values for cadmium as a function of pH.  
[Tabulated values pertain to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength ( $< 0.1$  M), low humic material concentrations ( $< 5$  mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

| $K_d$ (ml/g) | pH    |       |        |
|--------------|-------|-------|--------|
|              | 3 - 5 | 5 - 8 | 8 - 10 |
| Minimum      | 1     | 8     | 50     |
| Maximum      | 130   | 4,000 | 12,600 |

#### 5.2.6.2.2 Limits of $K_d$ Values with Respect to CEC

The effect of CEC on cadmium  $K_d$  values was evaluated using the data presented in Appendix C. Of the 174 cadmium  $K_d$  values in the data set presented in Appendix C, only 22 values had associated CEC data. The correlation coefficient describing the linear relationship between cadmium  $K_d$  values and CEC was 0.40, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between CEC and cadmium  $K_d$  values because cadmium can adsorb to minerals via cation exchange.

#### 5.2.6.2.3 Limits of $K_d$ Values with Respect to Clay Content

The effect of clay content on cadmium  $K_d$  values was evaluated using the data presented in Appendix C. Of the 174 cadmium  $K_d$  values in the data set presented in Appendix C, 64 values had associated clay content data. The correlation coefficient describing the linear relationship between cadmium  $K_d$  values and clay content was -0.04, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between clay content and cadmium  $K_d$  values, because clay content is often highly correlated to CEC, which in turn may be correlated to the number of sites available for cadmium adsorption.

#### 5.2.6.2.4 Limits of $K_d$ Values with Respect to Concentration of Organic Matter

The effect of organic matter concentration, as approximated by total organic carbon, on cadmium  $K_d$  values was evaluated using the data presented in Appendix C. Of the 174 cadmium  $K_d$  values in the data set presented in Appendix C, 63 values had associated total organic carbon concentration data. The correlation coefficient describing the linear relationship between cadmium  $K_d$  values and total organic carbon concentration was 0.20, which is nonsignificant at the 5 percent level of probability. It was anticipated that there would be a positive correlation between total organic carbon concentration and cadmium  $K_d$  values because soil organic carbon can have extremely high CEC values, providing additional sorption sites for dissolved cadmium.

#### 5.2.6.2.5 Limits of $K_d$ Values with Respect to Dissolved Calcium, Magnesium, and Sulfide Concentrations, and Redox Conditions

Calcium, magnesium, and sulfide solution concentrations were rarely, if at all, reported in the experiments used to comprise the cadmium data set. It was anticipated that dissolved calcium and magnesium would compete with cadmium for adsorption sites, thereby decreasing  $K_d$  values. It was anticipated that sulfides would induce cadmium precipitation, thereby increasing cadmium  $K_d$  values. Similarly, low redox status was expected to provide an indirect measure of sulfide concentrations, which would in turn induce cadmium precipitation. Sulfides only exist in low redox environments; in high redox environments, the sulfides oxidize to sulfates that are less prone to form cadmium precipitates.



### 5.3 Cesium Geochemistry and $K_d$ Values

#### 5.3.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

The aqueous speciation of cesium in groundwater is among the simplest of the contaminants being considered in this study. Cesium forms few stable complexes and is likely to exist in groundwater as the uncomplexed  $\text{Cs}^+$  ion, which adsorbs rather strongly to most minerals, especially mica-like clay minerals. The extent to which adsorption will occur will depend on (1) the concentration of mica-like clays in the soil, and (2) the concentration of major cations, such as  $\text{K}^+$  which has a small ionic radius as  $\text{Cs}^+$ , that can effectively compete with  $\text{Cs}^+$  for adsorption sites.

#### 5.3.2 General Geochemistry

Cesium (Cs) exists in the environment in the +1 oxidation state. Stable cesium is ubiquitous in the environment with concentrations in soils ranging between 0.3 and 25 mg/kg (Lindsay, 1979). The only stable isotope of cesium is  $^{133}\text{Cs}$ . Fission products include 4 main cesium isotopes. Of these, only  $^{134}\text{Cs}$  [half life ( $t_{1/2}$ ) = 2.05 y],  $^{135}\text{Cs}$  ( $t_{1/2}$  =  $3 \times 10^6$  y), and  $^{137}\text{Cs}$  ( $t_{1/2}$  = 30.23 y) are at significant concentrations 10 y after separation from nuclear fuels (Schneider and Platt, 1974).

Contamination includes cesium-containing soils and cesium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination of soil, surface water, and/or groundwater by  $^{134}\text{Cs}$ ,  $^{135}\text{Cs}$  and/or  $^{137}\text{Cs}$  has been identified at 9 of the 45 Superfund National Priorities List (NPL) sites.

#### 5.3.3 Aqueous Speciation

There is little, if any, tendency for cesium to form aqueous complexes in soil/water environments. Thus, the formation of inorganic complexes is not a major influence on cesium speciation and the dominant aqueous species in most groundwater is the uncomplexed  $\text{Cs}^+$  ion. Baes and Mesmer (1976) report that cesium may be associated with  $\text{OH}^-$  ions in solution, but that the extent of this association cannot be estimated accurately. The uncomplexed  $\text{Cs}^+$  ion forms extremely weak aqueous complexes with sulfate, chloride, and nitrate. Cesium also can form weak complexes with humic materials, as shown by the following ranking of cations by their propensity to form complexes with humic materials (Bovard *et al.*, 1970):





Further, complexation of cesium by common industrial chelates (*e.g.*, EDTA) is believed to be poor due to their low stabilities and the presence of competing cations (*e.g.*,  $\text{Ca}^{2+}$ ) at appreciably higher concentrations than that of cesium. Therefore, aqueous complexation is not thought to greatly influence cesium behavior in most groundwater systems.

#### **5.3.4 Dissolution/Precipitation/Coprecipitation**

Neither precipitation nor coprecipitation are expected to affect the geochemistry of cesium in groundwater. The solubility of most cesium compounds in water is very high.

#### **5.3.5 Sorption/Desorption**

In general, most soils sorb cesium rather strongly (Ames and Rai, 1978). Some mica-like minerals, such as illite  $\{(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,\text{H}_2\text{O}]\}$  and vermiculite  $[(\text{Mg},\text{Fe},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2\cdot 4\text{H}_2\text{O}]$ , tend to intercalate (fix) cesium between their structural layers (Bruggenwert and Kamphorst, 1979; Douglas, 1989; Smith and Comans, 1996). These silicate minerals can be thought of as having a crystal lattice composed of continuous sheet structures. The distance between the silicate layers is controlled by the type of cation associated with the adsorption sites on the layers. Large hydrated cations, such as  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , tend to pry the layers further apart, whereas small hydrated cations, such as  $\text{K}^+$ , have the opposite effect. The interlayer distance between the sheets of mica-like minerals excludes the absorption of the majority of cations by size, while permitting the  $\text{Cs}^+$  ion to fit perfectly between the layers. Consequently, these mica-like minerals commonly exhibit a very high selectivity for  $\text{Cs}^+$  over other cations, including cations existing at much higher concentrations. Even a small amount (*e.g.*, 1-2 weight percent) of these mica-like minerals in a soil may strongly absorb a large amount of dissolved cesium (Coleman *et al.*, 1963; Douglas, 1989). Some researchers have considered the exchange of trace cesium on these mica-like minerals to be nearly irreversible (Douglas, 1989; Routson, 1973), meaning that cesium absorbs at a much faster rate than it desorbs.

The effect of cesium concentration and pH on cesium adsorption by a calcareous soil containing mica-like minerals has been studied by McHenry (1954). The data indicate that trace cesium concentrations are essentially completely adsorbed above pH 4.0. When placed in a high-salt solution, 4 M NaCl, only up to 75 percent of the trace cesium was adsorbed, and the adsorption was essentially independent of pH over a wide range. At cesium loadings on the soil of less than 1 percent of the soil CEC, the effect of competing cations on cesium adsorption was slight. Low concentrations of dissolved cesium are typical of cesium-contaminated areas. Thus competition may not play an important role in controlling cesium adsorption in most natural groundwater environments. The results of McHenry (1954) also indicate that trace concentrations of cesium were adsorbed to a greater degree and were more difficult to displace from the soil by competing cations than when the cesium was adsorbed at higher loadings.

Cesium may also adsorb to iron oxides (Schwertmann and Taylor, 1989). Iron oxides, unlike mica-like minerals, do not “fix” cesium. Instead they complex cesium to sites whose abundance is pH dependent; *i.e.*, iron oxides have variable charge surfaces. Iron oxides dominate the adsorption capacity of many soils in semi-tropical regions, such as the southeastern United States. In these soils, many mica-like minerals have been weathered away, leaving minerals with more pH-dependent charge. As the pH decreases, the number of negatively charged complexation sites also decreases. For example, Prout (1958) reported that cesium adsorption to iron-oxide dominated soils from South Carolina decreased dramatically when the suspension pH was less than 6.

Cesium adsorption to humic materials is generally quite weak (Bovard *et al.*, 1970). This is consistent with cation ranking listed above showing that cesium forms relatively weak complexes with organic matter.

### **5.3.6 Partition Coefficient, $K_d$ , Values**

#### **5.3.6.1 General Availability of $K_d$ Data**

Three generalized, simplifying assumptions were established for the selection of cesium  $K_d$  values for the look-up table. These assumptions were based on the findings of the literature review we conducted on the geochemical processes affecting cesium sorption.<sup>1</sup> The assumptions are as follows:

- Cesium adsorption occurs entirely by cation exchange, with the exception when mica-like minerals are present. Cation exchange capacity (CEC), a parameter that is frequently not measured, can be estimated by an empirical relationship with clay content and pH.
- Cesium adsorption into mica-like minerals occurs much more readily than desorption. Thus,  $K_d$  values, which are essentially always derived from adsorption studies, will greatly overestimate the degree to which cesium will desorb from these surfaces.
- Cesium concentrations in groundwater plumes are low enough, less than approximately  $10^{-7}$  M, such that cesium adsorption follows a linear isotherm.

These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are clearly compromised in systems with cesium concentrations greater than approximately  $10^{-7}$  M, ionic strength levels greater than about 0.1 M, and pH levels greater than about 10.5. These 3 assumptions will be discussed in more detail in the following sections.

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<sup>1</sup> Since the completion of our review and analysis of  $K_d$  data for the selected contaminants and radionuclides, the studies by Cygan *et al.* (1998), Fisher *et al.* (1999), and Oscarson and Hume (1998) were identified and may be of interest to the reader.

Based on the assumptions and limitation described in above, cesium  $K_d$  values and some important ancillary parameters that influence cation exchange were collected from the literature and tabulated. Data included in this table were from studies that reported  $K_d$  values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of: (1) low ionic strength ( $< 0.1$  M), (2) pH values between 4 and 10.5, (3) dissolved cesium concentrations less than  $10^{-7}$  M, (4) low humic material concentrations ( $< 5$  mg/l), and (5) no organic chelates (*e.g.*, EDTA). Initially, attempts were made to include in the  $K_d$  data set all the key aqueous and solid phase parameters identified above. The key parameters included aluminum/iron-oxide mineral concentration, CEC, clay content, potassium concentration, mica-like mineral content, ammonium concentration, and pH. The ancillary parameters for which data could be found in the literature that were included in these tables were clay content, mica content, pH, CEC, surface area, and solution cesium concentrations. This cesium data set included 176 cesium  $K_d$  values. The descriptive statistics of the cesium  $K_d$  data set are presented in Appendix D.

#### 5.3.6.2 Look-Up Tables

Linear regression analyses were conducted with data collected from the literature. These analyses were used as guidance for selecting appropriate  $K_d$  values for the look-up table. The  $K_d$  values used in the look-up tables could not be based entirely on statistical consideration because the statistical analysis results were occasionally nonsensible. For example, the data showed a negative correlation between pH and CEC, and pH and cesium  $K_d$  values. These trends contradict well established principles of surface chemistry. Instead, the statistical analysis was used to provide guidance as to the approximate range of values to use and to identify meaningful trends between the cesium  $K_d$  values and the solid phase parameters. Thus, the  $K_d$  values included in the look-up table were in part selected based on professional judgment. Again, only low-ionic strength solutions, such as groundwaters, were considered; thus no solution variables were included.

Two look-up tables containing cesium  $K_d$  values were created. The first table is for systems containing low concentrations of mica-like minerals: less than about 5 percent of the clay-size fraction (Table 5.5). The second table is for systems containing high concentrations of mica-like minerals (Table 5.6). For both tables, the user will be able to reduce the range of possible cesium  $K_d$  values with knowledge of either the CEC or the clay content. A detailed description of the assumptions and the procedures used in coming up with these values is presented in Appendix D.

**Table 5.5.** Estimated range of  $K_d$  values (ml/g) for cesium based on CEC or clay content for systems containing <5 percent mica-like minerals in clay-size fraction and  $<10^{-9}$  M aqueous cesium. [Table pertains to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength ( $<0.1$  M), low humic material concentrations ( $<5$  mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

| $K_d$ (ml/g) | CEC (meq/100 g) / Clay Content (wt.%) |                 |                   |
|--------------|---------------------------------------|-----------------|-------------------|
|              | <3 / <4                               | 3 - 10 / 4 - 20 | 10 - 50 / 20 - 60 |
| Minimum      | 10                                    | 30              | 80                |
| Maximum      | 3,500                                 | 9,000           | 26,700            |

**Table 5.6.** Estimated range of  $K_d$  values (ml/g) for cesium based on CEC or clay content for systems containing >5 percent mica-like minerals in clay-size fraction and  $<10^{-9}$  M aqueous cesium. [Table pertains to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength ( $<0.1$  M), low humic material concentrations ( $<5$  mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

| $K_d$ (ml/g) | CEC (meq/100 g) / Clay Content (wt.%) |                 |                   |
|--------------|---------------------------------------|-----------------|-------------------|
|              | <3 / <4                               | 3 - 10 / 4 - 20 | 10 - 50 / 20 - 60 |
| Minimum      | 30                                    | 70              | 210               |
| Maximum      | 9,000                                 | 22,000          | 66,700            |

#### 5.3.6.2.1 Limits of $K_d$ Values with Respect to pH

Of the 177 cesium  $K_d$  values obtained from the literature, 139 of them had associated pH values for the system under consideration (Appendix D). The average pH of the systems described in the data set was pH 7.4, ranging from pH 2.4 to 10.2. The correlation coefficient ( $r$ ) between pH and cesium  $K_d$  values was 0.05. This is clearly an insignificant correlation. This poor correlation may be attributed to the fact that other soil properties having a greater impact on cesium  $K_d$  values were not held constant throughout this data set.

#### 5.3.6.2.2 Limits of $K_d$ Values with Respect to Potassium, Ammonium, and Aluminum/Iron-Oxides Concentrations

Potassium, ammonium, and aluminum/iron-oxide mineral concentrations were rarely, if at all, reported in the experiments used to comprise the cesium  $K_d$  data set (Appendix D). It was anticipated that dissolved potassium and ammonium would compete with cesium for adsorption sites, thereby decreasing  $K_d$  values. The presence of aluminum and/or iron oxides in the solid phase was expected to increase cesium  $K_d$  values.

### 5.4 Chromium Geochemistry and $K_d$ Values

#### 5.4.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

A plume containing high concentrations of chromium is more likely to be composed of Cr(VI) than Cr(III) because the former is less likely to adsorb or precipitate to the solid phase. Chromium(VI) is also appreciably more toxic than Cr(III). It exhibits significant subsurface mobility in neutral and basic pH environments. In acid environments, Cr(VI) may be moderately adsorbed by pH-dependent charge minerals, such as iron- and aluminum-oxide minerals. The reduction of Cr(VI) to Cr(III) by ferrous iron, organic matter, and microbes is generally quite rapid whereas the oxidation of Cr(III) to Cr(VI) by soil manganese oxides or dissolved oxygen is kinetically slower. The most important aqueous- and solid-phase parameters controlling retardation of chromium include redox status, pH, and the concentrations of aluminum- and iron-oxide minerals and organic matter.

#### 5.4.2 General Geochemistry

Chromium is found in the environment primarily in the +3 and +6 oxidation states. The geochemical behavior and biological toxicity of chromium in these 2 oxidation states are profoundly different. Chromium(VI) tends to be soluble, forms anionic or neutral dissolved species, can be very mobile, and is acutely toxic (Nriagu and Nieboer, 1988). In contrast, Cr(III) tends to precipitate, forms cationic dissolved species, is immobile under moderately alkaline to slightly acidic conditions, and is relatively nontoxic. The primary human activities leading to the introduction of chromium into the environment are

ore processing, plating operations, and manufacturing (reviewed by Nriagu and Nieboer, 1988). Discussions of the production, uses, and toxicology of chromium have been presented by Nriagu and Nieboer (1988). Good review articles describing the geochemistry of chromium have been written by Rai *et al.* (1988), Palmer and Wittbrodt (1991), Richard and Bourg (1991), and Palmer and Puls (1994). A critical review of the thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides was published by Ball and Nordstrom (1998).

#### 5.4.3 Aqueous Speciation

Chromium exists in the +2, +3, and +6 oxidation states in water, of which only the +3 and +6 states are found in the environment. Chromium(III) exists over a wide range of pH and Eh conditions, whereas Cr(VI) exists only under strongly oxidizing conditions. According to Baes and Mesmer (1976), Cr(III) exists predominantly as  $\text{Cr}^{3+}$  below pH 3.5 in a Cr(III)-H<sub>2</sub>O system. With increasing pH, hydrolysis of  $\text{Cr}^{3+}$  yields  $\text{CrOH}^{2+}$ ,  $\text{Cr(OH)}_2^+$ ,  $\text{Cr(OH)}_3^{\text{aq}}$ , and  $\text{Cr(OH)}_4^-$ ,  $\text{Cr}_2(\text{OH})_2^{4+}$ , and  $\text{Cr}_3(\text{OH})_4^{5+}$ . At higher chromium concentrations, polynuclear species, such as  $\text{Cr}_2(\text{OH})_2^{4+}$  and  $\text{Cr}_3(\text{OH})_4^{5+}$ , can form slowly at 25°C (Baes and Mesmer, 1976). Chromium(VI) hydrolyses extensively, forming primarily anionic species. These species are  $\text{HCrO}_4^-$  (bichromate),  $\text{CrO}_4^{2-}$  (chromate), and  $\text{Cr}_2\text{O}_7^{2-}$  (dichromate) (Baes and Mesmer, 1976; Palmer and Wittbrodt, 1991; Richard and Bourg, 1991). Palmer and Puls (1994) presented some Cr(VI) speciation diagrams representative of groundwater conditions. They showed that above pH 6.5,  $\text{CrO}_4^{2-}$  generally dominates. Below pH 6.5,  $\text{HCrO}_4^-$  dominates when the total concentration of dissolved Cr(VI) is low (<30 mM). When Cr(VI) concentrations are greater than 30 mM,  $\text{Cr}_2\text{O}_7^{2-}$  is the dominant aqueous species relative to  $\text{HCrO}_4^-$  at acidic conditions (Palmer and Puls, 1994). These results are consistent with those of Baes and Mesmer (1976).

#### 5.4.4 Dissolution/Precipitation/Coprecipitation

Several investigators have presented evidence suggesting the formation of solubility-controlling solids of Cr(III) in soils. Rai and Zachara (1984) concluded that most Cr(III) solubility-controlling solids in nature are either  $\text{Cr(OH)}_3$  or Cr(III) coprecipitated with iron oxides. Their conclusion was supported by 3 observations: (1) the thermodynamic treatment of the data where the solubility of chromite ( $\text{FeCr}_2\text{O}_4$ ) is predicted to be the lowest among the chromium minerals for which data are available (Hem, 1977), (2) the similarity of Cr(III) and Fe(III) ionic radii, and (3) the observations that aqueous Cr(III) is removed by  $\text{Fe(OH)}_3$  precipitation and that chromium during weathering is found to associate with ferric-rich materials (Nakayama *et al.*, 1981). Hem (1977) reported that the total chromium concentration in groundwater beneath Paradise Valley, Arizona was close to the solubility of  $\text{Cr}_2\text{O}_3$ . Because Cr(III) minerals are sparingly soluble, the aqueous concentration of Cr(III) should be less than EPA's maximum concentration level (MCL) for chromium (0.1 mg/l) between slightly acid to moderately alkaline conditions (Palmer and Puls, 1994).

Several Cr(VI)-containing mineral phases may be present at chromium-contaminated sites. Palmer and Wittbrodt (1990) identified  $\text{PbCrO}_4$  (crocoite),  $\text{PbCrO}_4 \cdot \text{H}_2\text{O}$  (iranite), and  $\text{K}_2\text{CrO}_4$  (tarapacaite) in

chromium sludge from a plating facility. They also reported that  $\text{BaCrO}_4$  formed a complete solid solution with  $\text{BaSO}_4$ . They concluded that these solid solutions can be a major impediment to the remediation of chromium-contaminated sites by pump-and-treat technologies.

Chromium(VI) is a strong oxidant and is rapidly reduced in the presence of such common electron donors as aqueous Fe(II), ferrous iron minerals, reduced sulfur, microbes, and organic matter (Bartlett and Kimble, 1976; Nakayama *et al.*, 1981). Studies indicate that Cr(VI) can be reduced to Cr(III) by ferrous iron derived from magnetite ( $\text{Fe}_3\text{O}_4$ ) and ilmenite ( $\text{FeTiO}_3$ ) (White and Hochella, 1989), hematite ( $\text{Fe}_2\text{O}_3$ ) (Eary and Rai, 1989),<sup>1</sup> and pyrite ( $\text{FeS}_2$ ) (Blowes and Ptacek, 1992).

The reduction of Cr(VI) by Fe(II) is very rapid. The reaction can go to completion in a matter of minutes (Eary and Rai, 1989). The rate of reduction of Cr(VI) increases with decreasing pH and increasing initial Cr(VI) and reductant concentrations (Palmer and Puls, 1994). Interestingly, this reaction does not appear to be slowed by the presence of dissolved oxygen (Eary and Rai, 1989). When the pH is greater than 4, Cr(III) can precipitate with Fe(III) to form a solid solution with the general composition  $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$  (Sass and Rai, 1987). The solubility of chromium in this solid solution decreases as the mole fraction of Fe(III) increases. The oxidation reaction proceeds much more slowly than the reduction reaction; the former reaction requires months for completion (Eary and Rai, 1987; Palmer and Puls, 1994). Only 2 constituents in the environment are known to oxidize Cr(III): dissolved oxygen and manganese-dioxide minerals [*e.g.*, pyrolusite ( $\beta\text{-MnO}_2$ )]. Eary and Rai (1987) reported that the rate of Cr(III) oxidation was much greater in the presence of manganese-dioxide minerals than dissolved oxygen.

#### 5.4.5 Sorption/Desorption

The extent to which Cr(III) sorbs to soils is appreciably greater than that of Cr(VI) because the former exists in groundwater as a cation, primarily as  $\text{Cr}^{3+}$  (and its complexed species), whereas the latter exists as an anion, primarily as  $\text{CrO}_4^{2-}$  or  $\text{HCrO}_4^-$ . Most information on Cr(VI) adsorption comes from studies with pure mineral phases (Davis and Leckie, 1980; Griffin *et al.*, 1977; Leckie *et al.*, 1980). These studies suggest that Cr(VI) adsorbs strongly to gibbsite ( $\alpha\text{-Al}_2\text{O}_3$ ) and amorphous iron oxide [ $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}(\text{am})$ ] at low to medium pH values (pH 2 to 7) and adsorbs weakly to silica ( $\text{SiO}_2$ ) at all but very low pH values (Davis and Leckie, 1980; Griffin *et al.*, 1977; Leckie *et al.*, 1980). These results can be explained by considering the isoelectric points (IEP)<sup>2</sup> of these minerals. When the pH of the system is greater than the isoelectric point, the mineral has a net negative charge. When the pH is

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<sup>1</sup> Eary and Rai (1989) attributed the reduction of Cr(VI) to Cr(III) by hematite ( $\text{Fe}_2\text{O}_3$ ) as containing having trace quantities of Fe(II).

<sup>2</sup> The isoelectric point (IEP) of a mineral is the pH at which it has a net surface charge of zero. More precisely, it is the pH at which the particle is electrokinetically uncharged.

below the isoelectric point, the mineral has a net positive charge. Hence, anion adsorption generally increases as the pH becomes progressively lower than the isoelectric point. The isoelectric point of gibbsite ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) is 9.1, amorphous iron oxide [ $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (am)] is 8.1, and silica is 2.0 (Stumm and Morgan, 1981).

The presence of competing and, less commonly, complexing ions may significantly alter chromate adsorption. Although sulfate is adsorbed less strongly on  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (am) than chromate, sulfate may compete for adsorption sites when present in higher concentration (Leckie *et al.*, 1980). Phosphate exhibits a greater competitive effect on chromate adsorption (MacNaughton, 1977), reducing sorption by around 50 percent when present at equal normality. Information on effects of complexing ions on Cr(VI) sorption is almost nonexistent, though adsorption of ion pairs [*e.g.*,  $\text{CaCrO}_4^{\text{II}}$ (aq) and  $\text{KHCrO}_4^{\text{II}}$ (aq)] is suggested as 1 possible mechanism for removal of Cr(VI) by  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (am) (Leckie *et al.*, 1980).

Adsorption of Cr(III) to soils has received only a nominal amount of research attention. The reason for this may be that sorption of Cr(III) by soil is commonly ascribed to solid phase formation. Chromium(III) rapidly hydrolyzes, and precipitates as the hydroxide  $\text{Cr}(\text{OH})_3$  and/or coprecipitates with  $\text{Fe}(\text{OH})_3$  (Artiola and Fuller, 1979; Hem, 1977,). Adsorption may be an especially important mechanism of sorption at lower pH (pH <4.5) and total chromium concentrations (< $10^{-6}$  M). Limited studies infer that Cr(III), like other +3 cationic metals, is strongly and specifically absorbed by soil iron and manganese oxides (Korte *et al.*, 1976). However, when Cr(III) is present in solution at high concentrations, it may undergo exchange reactions with aluminosilicates (Griffin *et al.*, 1977). Chromium(III) adsorption may also be influenced by the presence of manganese-oxide minerals. Manganese oxides may catalyze oxidation to Cr(VI), thereby decreasing the tendency for chromium to adsorb to the soils (Bartlett and James, 1979; Nakayama *et al.*, 1981).

#### **5.4.6 Partition Coefficient, $K_d$ , Values**

##### **5.4.6.1 General Availability of $K_d$ Data**

The review of chromium  $K_d$  data obtained for a number of soils (Appendix E) indicated that a number of factors influence the adsorption behavior of chromium. These factors and their effects on chromium adsorption on soils were used as the basis for generating a look-up table. These factors are:

- Concentrations of Cr(III) in soil solutions are typically controlled by dissolution/precipitation reactions.
- Increasing pH decreases adsorption (decrease in  $K_d$ ) of Cr(VI) on minerals and soils. The data are quantified for only a limited number of soils.



- The redox state of the soil affects chromium adsorption. Ferrous iron associated with iron oxide/hydroxide minerals in soils can reduce Cr(VI) which results in precipitation (higher  $K_d$ ). Soils containing Mn oxides oxidize Cr(III) into Cr(VI) form thus resulting in lower  $K_d$  values. The relation between oxide/hydroxide contents of iron and manganese and their effects on  $K_d$  have not been adequately quantified except for a few soils.
- The presence of competing anions reduce Cr(VI) adsorption. These effects have been quantified as a function of pH for only 2 soils.

The factors which influence chromium adsorption were identified from studies by Leckie *et al.* (1980), Davis and Leckie (1980), Griffin *et al.* (1977), and Rai *et al.* (1986), and studies discussed below. A description and assessment of these data are provided in Appendix E.

Adsorption data also show that iron and manganese oxide contents of soils significantly affect the adsorption of Cr(VI) on soils (Korte *et al.*, 1976). However, these investigators did not publish either  $K_d$  values or any correlative relationships between  $K_d$  and the oxide contents. Studies by Stollenwerk and Grove (1985) and Sheppard *et al.* (1987) using soils showed that  $K_d$  decreases as a function of increasing equilibrium concentration of Cr(VI). Another study conducted by Rai *et al.* (1988) on 4 different soils confirmed that  $K_d$  values decrease with increasing equilibrium Cr(VI) concentration. The adsorption data obtained by Rai *et al.* (1988) also showed that quantities of sodium dithionite-citrate-bicarbonate (DCB) extractable iron content of soils is a good indicator of a soil's ability to reduce Cr(VI) to the Cr(III) oxidation state. The reduced Cr has been shown to coprecipitate with ferric hydroxide. Therefore, observed removal of Cr(VI) from solution when contacted with chromium-reductive soils may stem from both adsorption and precipitation reactions. Similarly, Rai *et al.* (1988) also showed that certain soils containing manganese oxides may oxidize Cr(III) to Cr(VI). Depending on solution concentrations, the oxidized form (+6) of chromium may also precipitate in the form of  $\text{Ba}(\text{S,Cr})\text{O}_4$ . Such complex geochemical behavior chromium in soils implies that depending on the properties of a soil, the measured  $K_d$  values may reflect both adsorption and precipitation reactions.

Adsorption studies have shown that competing anions such as  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}/\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , significantly reduce Cr(VI) adsorption on oxide minerals and soils (Leckie *et al.*, 1980; MacNaughton, 1977; Rai *et al.*, 1986; Rai *et al.*, 1988; Stollenwerk and Grove, 1985).

The data regarding the effects of soil organic matter on Cr(VI) adsorption are rather sparse. In 1 study (Stollenwerk and Grove, 1985) which evaluated the effects of soil organic matter on adsorption of Cr(VI), the results indicated that organic matter did not influence Cr(VI) adsorption properties (see Appendix E).

#### 5.4.6.2 $K_d$ Look-Up Tables

Among all available data for Cr(VI) adsorption on soils, the most extensive data set was developed by Rai *et al.* (1988). These investigators studied the adsorption behavior of 4 different well-characterized subsurface soil samples. They investigated the adsorption behavior of Cr(VI) on these 4 soil samples as a function of pH. Additionally, they also investigated the effects of competing anions such as  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}/\text{HCO}_3^-$ . The adsorption data developed by these investigators was used to calculate the  $K_d$  values (Appendix E). These  $K_d$  values were used as the basis to develop the look-up Table 5.7.

#### 5.4.6.2.1 Limits of $K_d$ Values with Respect to pH

Natural soil pH typically ranges from about 4 to 11 (Richards, 1954). The 2 most common methods of measuring soil pH are either using a soil paste or a saturation extract. The standard procedure for obtaining saturation extracts from soils has been described by Rhoades (1996). The saturation extracts are obtained by saturating and equilibrating the soil with distilled water followed by collection using vacuum filtration. Saturation extracts are usually used to determine the pH, the electrical conductivity, and dissolved salts in soils.

The narrow pH ranges in the look-up table (Table 5.7) were selected from the observed rate of change of  $K_d$  with pH. The  $K_d$  values for all 4 soils were observed to decline with increasing pH and at pH values beyond about 9,  $K_d$  values for Cr(VI) are  $\leq 1$  ml/g (see Appendix E).

#### 5.4.6.2.2 Limits of $K_d$ Values with Respect to Extractable Iron Content

The soil characterization data provided by Rai *et al.* (1988) indicate the soils with DCB extractable iron contents above  $\sim 0.3$  mmol/g can reduce Cr(VI) to Cr(III). Therefore the measured  $K_d$  values for such soils reflect both redox-mediated precipitation and adsorption phenomena. The data also show that soils with DCB extractable iron contents of about 0.25 mmol/g or less do not appear to reduce Cr(VI). Therefore, 3 ranges of DCB extractable iron contents were selected which represent the categories of soils that definitely reduce ( $\geq 0.3$  mmol/g), probably reduce (0.26 - 0.29 mmol/g), and do not reduce ( $\leq 0.25$  mmol/g) Cr(VI) to Cr(III) form.

#### 5.4.6.2.3 Limits of $K_d$ Values with Respect to Competing Anion Concentrations

The adsorption data (Rai *et al.*, 1988) show that when total sulfate concentration in solution is about  $2 \times 10^{-3}$  M (191.5 mg/l), the chromium  $K_d$  values are reduced by about an order of magnitude as compared to a noncompetitive condition. Therefore, a sulfate concentration of about  $2 \times 10^{-3}$  M (191.5 mg/l) has been used as a limit at which an order of magnitude reduction in  $K_d$  values are expected. Four ranges of soluble sulfate concentrations (0 - 1.9, 2 - 18.9, 19 - 189, and  $\geq 190$  mg/l) have been used to develop the look-up table. The soluble sulfate concentrations in soils can be assessed from saturation extracts (Richards, 1954).

**Table 5.7.** Estimated range of  $K_d$  values for chromium (VI) as a function of soil pH, extractable iron content, and soluble sulfate. (Data analysis and generation of the table of  $K_d$  values are described in Appendix E.)

|                             |                       | pH                          |             |        |                             |             |        |                             |             |        |                             |             |        |
|-----------------------------|-----------------------|-----------------------------|-------------|--------|-----------------------------|-------------|--------|-----------------------------|-------------|--------|-----------------------------|-------------|--------|
|                             |                       | 4.1 - 5.0                   |             |        | 5.1 - 6.0                   |             |        | 6.1 - 7.0                   |             |        | ≥ 7.1                       |             |        |
| Soluble Sulfate Conc (mg/l) | K <sub>d</sub> (ml/g) | DCB Extractable Fe (mmol/g) |             |        | DCB Extractable Fe (mmol/g) |             |        | DCB Extractable Fe (mmol/g) |             |        | DCB Extractable Fe (mmol/g) |             |        |
|                             |                       | ≤ 0.25                      | 0.26 - 0.29 | ≥ 0.30 | ≤ 0.25                      | 0.26 - 0.29 | ≥ 0.30 | ≤ 0.25                      | 0.26 - 0.29 | ≥ 0.30 | ≤ 0.25                      | 0.26 - 0.29 | ≥ 0.30 |
| 0 - 1.9                     | Min                   | 25                          | 400         | 990    | 20                          | 190         | 390    | 8                           | 70          | 80     | 0                           | 0           | 1      |
|                             | Max                   | 35                          | 700         | 1770   | 34                          | 380         | 920    | 22                          | 180         | 350    | 7                           | 30          | 60     |
| 2 - 18.9                    | Min                   | 12                          | 190         | 460    | 10                          | 90          | 180    | 4                           | 30          | 40     | 0                           | 0           | 1      |
|                             | Max                   | 15                          | 330         | 820    | 15                          | 180         | 430    | 10                          | 80          | 160    | 3                           | 14          | 30     |
| 19 - 189                    | Min                   | 5                           | 90          | 210    | 4                           | 40          | 80     | 2                           | 15          | 20     | 0                           | 0           | 0      |
|                             | Max                   | 8                           | 150         | 380    | 7                           | 80          | 200    | 5                           | 40          | 75     | 2                           | 7           | 13     |
| ≥ 190                       | Min                   | 3                           | 40          | 100    | 2                           | 20          | 40     | 1                           | 7           | 8      | 0                           | 0           | 0      |
|                             | Max                   | 4                           | 70          | 180    | 3                           | 40          | 90     | 2                           | 20          | 35     | 1                           | 3           | 6      |

## 5.5 Lead Geochemistry and $K_d$ Values

### 5.5.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Lead has 3 known oxidation states, 0, +2, and +4, and the most common redox state encountered in the environment is the divalent form. Total dissolved lead concentrations in natural waters are very low ( $\sim 10^{-8}$  M). Dissolved lead in natural systems may exist in free ionic form and also as hydrolytic and complex species. Speciation calculations show that at pH values exceeding 7, aqueous lead exists mainly as carbonate complexes [ $\text{PbCO}_3^{\text{aq}}$ ], and  $\text{Pb}(\text{CO}_3)_2^{2-}$ ]. Important factors that control aqueous speciation of lead include pH, the types and concentrations of complexing ligands and major cationic constituents, and the magnitude of stability constants for lead-ligand aqueous complexes.

A number of studies and calculations show that under oxidizing conditions depending on pH and ligand concentrations, pure-phase lead solids, such as  $\text{PbCO}_3$ ,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ,  $\text{PbSO}_4$ ,  $\text{Pb}_5(\text{PO}_4)_3(\text{Cl})$ , and  $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ , may control aqueous lead concentrations. Under reducing conditions, galena ( $\text{PbS}$ ) may regulate the concentrations of dissolved lead. It is also possible that lead concentrations in some natural systems are being controlled by solid solution phases such as barite ( $\text{Ba}_{(1-x)}\text{Pb}_x\text{SO}_4$ ), apatite [ $\text{Ca}_{(1-x)}\text{Pb}_x(\text{PO}_4)_3\text{OH}$ ], calcite ( $\text{Ca}_{(1-x)}\text{Pb}_x\text{CO}_3$ ), and iron sulfides ( $\text{Fe}_{(1-x)}\text{Pb}_x\text{S}$ ).

Lead is known to adsorb onto soil constituent surfaces such as clay, oxides, hydroxides, oxyhydroxides, and organic matter. In the absence of a distinct lead solid phase, natural lead concentrations would be controlled by adsorption/desorption reactions. Adsorption data show that lead has very strong adsorption affinity for soils as compared to a number of first transition metals. Lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils. Properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have greater effect on lead adsorption than soil pH.

### 5.5.2 General Geochemistry

Lead is an ubiquitous heavy metal and its concentration in uncontaminated soil ranges from 2 to 200 mg/kg and averages 16 mg/kg (Bowen, 1979). Annual anthropogenic lead input into soils has been estimated to be from 0.04 to 4 micro g/kg (Ter Haar *et al.*, 1967). In contaminated soils, lead concentrations may be as high as 18 percent by weight (Mattigod and Page, 1983; Ruby *et al.*, 1994). Lead in nature occurs in 4 stable isotopic forms ( $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ ). The isotopes,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$  are the stable end products of the  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  thorium decay series, respectively (Robbins, 1980). Additionally, heavier isotopes of lead ( $^{210}\text{Pb}$ ,  $^{211}\text{Pb}$ ,  $^{212}\text{Pb}$ , and  $^{214}\text{Pb}$ ) are known to occur in nature as intermediate products of uranium and thorium decay (Robbins, 1978). The

most common valence state of lead encountered in the environment is the divalent form (Baes and Mesmer, 1976). Extensive studies of lead biogeochemistry have been conducted due to its known adverse effects on organisms (Hammond, 1977). Comprehensive descriptions of environmental chemistry of lead have been published by Boggess and Wixson (1977) and Nriagu (1978).

### 5.5.3 Aqueous Speciation

Lead exhibits typical amphoteric<sup>1</sup> metal ion behavior by forming hydrolytic species (Baes and Mesmer, 1976). Formation of monomeric hydrolytic species, such as  $\text{PbOH}^+$ ,  $\text{Pb(OH)}_2^0(\text{aq})$  and  $\text{Pb(OH)}_3^-$ , is well established. Although several polymeric hydrolytic species such as  $\text{Pb}_2\text{OH}^{3+}$ ,  $\text{Pb}_3(\text{OH})_3^{3+}$ ,  $\text{Pb}_4(\text{OH})_4^{4+}$ , and  $\text{Pb}_6(\text{OH})_8^{4+}$  are known to form at high lead concentrations, calculations show that these types of species are unlikely to form at concentrations of dissolved lead ( $\sim 10^{-9}$  M) typically encountered even in contaminated environments (Rickard and Nriagu, 1978). These investigators also showed that computation models of speciation of dissolved lead in fresh- or seawater predicted that at pH values exceeding about 6.5, the dominant species are lead-carbonate complexes. Lead is known to form aqueous complexes with inorganic ligands such as carbonate, chloride, fluoride, nitrate, and sulfate.

To examine the distribution of dissolved lead species in natural waters, MINTEQA2 model calculations were completed using the water composition described in Table 5.1. The total lead concentration was assumed to be 1 micro g/l based on the data for natural waters tabulated by Duram *et al.* (1971) and Hem (1985). A total of 21 aqueous species (uncomplexed  $\text{Pb}^{2+}$ , and 20 complex species, listed in Table 5.8) were used in the computation. Results of the computation are plotted as a species distribution diagram (Figure 5.2). The data show that, under low pH (<6) conditions, free ionic  $\text{Pb}^{2+}$  appears to be the dominant species, and the neutral species,  $\text{PbSO}_4^0(\text{aq})$ , accounts for about 5 percent of the total dissolved lead. Within the pH range of 6.5 to 7.5, the main species of lead appear to be free ionic species,  $\text{Pb}^{2+}$ , and the neutral complex species,  $\text{PbCO}_3^0(\text{aq})$  with minor percentage of the species consisting of  $\text{PbHCO}_3^+$  (about 15 percent),  $\text{PbSO}_4^0(\text{aq})$  (<5 percent), and  $\text{PbOH}^+$  (<5 percent). Between the pH range 7 to 9, the neutral complex species  $\text{PbCO}_3^0(\text{aq})$  dominates dissolved lead speciation. At pH values exceeding 9, in addition to  $\text{PbCO}_3^0(\text{aq})$ , a significant fraction of soluble lead is present as the anionic carbonate complex,  $\text{Pb(CO}_3)_2^{2-}$ . These calculations also confirm Rickard and Nriagu's (1978) observation that polymeric species are not significant in the chemistry of lead in natural waters. The species distribution illustrated in Figure 5.2 does not change if the concentration of total dissolved lead is increased from 1 to 1,000 micro g/l.

This speciation calculation demonstrates that the important factors that control aqueous speciation of lead include pH and the types of complexing ligands. Aqueous speciation of lead has a direct bearing

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<sup>1</sup> Amphoteric behavior is the ability of an aqueous complex or solid material to have a negative, neutral, or positive charge.

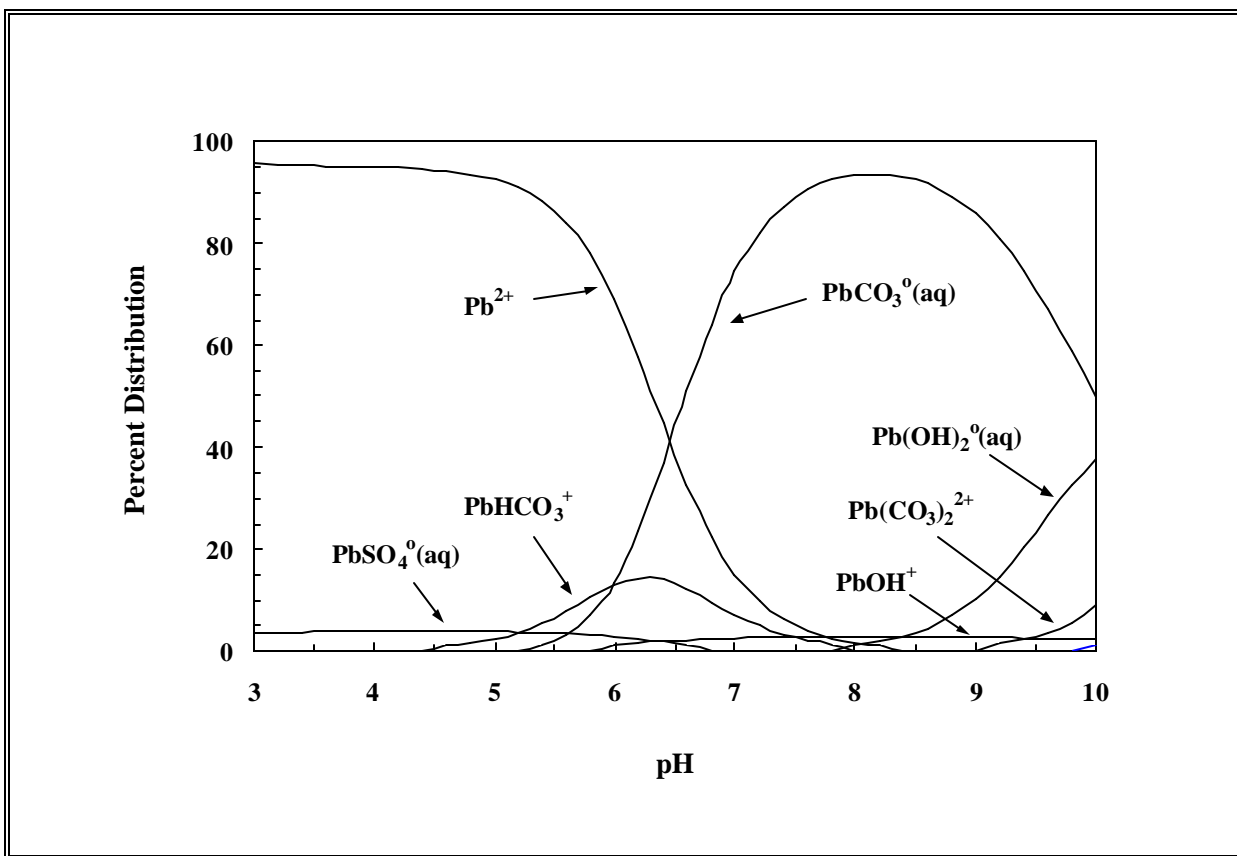
on dissolution/precipitation of lead-solid phases and the adsorption/desorption reactions. Complexation enhances the solubility of lead-bearing solid phases. This enhancement in solubility is dependent on the strength of complexation [indicated by the magnitude of stability constant] and the total concentrations of complexing ligands. Also, as will be discussed shortly, adsorption of lead is affected by the type, charge, and the concentration of lead complexes present in solution. Cationic lead species, especially  $\text{Pb}^{2+}$  and its hydrolysis species, adsorb more commonly than anionic lead complexes.

#### ***5.5.4 Dissolution/Precipitation/Coprecipitation***

Lead solids in the environment may occur in a number of mineral forms (Rickard and Nriagu 1978; Mattigod *et al.*, 1986; Zimdahl and Hassett, 1977). However, these authors have identified a limited number of secondary lead minerals that may control the concentrations of dissolved lead in soil/water environments. If the concentration of dissolved lead in a pore water or groundwater exceeds the solubility of any of these phases, the lead-containing solid phase will precipitate and thus control the maximum concentration of lead that could occur in the aqueous phase. According to Rickard and Nriagu (1978), under oxidizing conditions, depending on pH and ligand concentrations, cerussite ( $\text{PbCO}_3$ ), hydrocerussite [ $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ ], anglesite ( $\text{PbSO}_4$ ), or chloropyromorphite [ $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ] may control aqueous lead concentrations. A review paper by McLean and Bledsoe (1992) included data which showed that lead concentrations in a calcareous soil was controlled by lead-phosphate compounds at lower pH and by mixed mineral phases at pH values exceeding 7.5. A study conducted by Mattigod *et al.* (1986) indicated that the mineral leadhillite [ $\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$ ] may be the solubility controlling solid for lead in a mine-waste contaminated soil.

**Table 5.8.** Lead aqueous species included in the speciation calculations.

| Aqueous Species   |
|---|
| $\text{Pb}^{2+}$  |
| $\text{PbOH}^+$ , $\text{Pb}(\text{OH})_2^{\text{aq}}$ , $\text{Pb}(\text{OH})_3^-$ , $\text{Pb}(\text{OH})_4^{2-}$<br>$\text{Pb}_2(\text{OH})_3^+$ , $\text{Pb}_3(\text{OH})_3^{3+}$ |
| $\text{PbCO}_3^{\text{aq}}$ , $\text{Pb}(\text{CO}_3)_2^{2-}$ , $\text{PbHCO}_3^+$  |
| $\text{PbSO}_4^{\text{aq}}$ , $\text{Pb}(\text{SO}_4)_2^{2-}$   |
| $\text{PbNO}_3^+$   |
| $\text{PbCl}^+$ , $\text{PbCl}_2^{\text{aq}}$ , $\text{PbCl}_3^-$ , $\text{PbCl}_4^{2-}$  |
| $\text{PbF}^+$ , $\text{PbF}_2^{\text{aq}}$ , $\text{PbF}_3^-$ , $\text{PbF}_4^{2-}$  |



**Figure 5.2.** Calculated distribution of lead aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved lead.]

Lead may also exist in soils as solid-solution phases. Solid solutions are defined as solid phases in which a minor element will substitute for a major element in the mineral structure. Depending on the degree of substitution and the overall solubility of the solid-solution phase, the equilibrium solubility of the minor element in the solid solution phase will be less than the solubility of the solid phase containing only the minor element (pure phase). For instance, lead may occur as a minor replacement in barite [ $\text{Ba}_{(1-x)}\text{Pb}_x\text{SO}_4$ ], apatite [ $\text{Ca}_{(1-x)}\text{Pb}_x(\text{PO}_4)_3\text{OH}$ ], calcite [ $\text{Ca}_{(1-x)}\text{Pb}_x\text{CO}_3$ ], and iron sulfides, [ $\text{Fe}_{(1-x)}\text{Pb}_x\text{S}$ ] (Driesens, 1986; Goldschmidt, 1954; Nriagu and Moore, 1984; Rickard and Nriagu, 1978). Consequently, the equilibrium solubility of lead controlled by these phases will be less than the concentrations controlled by corresponding pure phases, namely  $\text{PbSO}_4$ ,  $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{PbCO}_3$ , and  $\text{PbS}$ , respectively.



Under reducing conditions, galena (PbS) may control the lead concentrations in the environment. Rickard and Nriagu (1978) calculated that, within the pH range of 6-9, the equilibrium solubility of galena would control total lead concentrations at levels less than approximately  $10^{-10}$  M (<21 ng/l). Therefore, if galena is present in a soil under reducing conditions, the aqueous concentrations of lead will be controlled at extremely low concentrations.

#### **5.5.5 Sorption/Desorption**

Lead is known to adsorb onto soil constituent surfaces such as clays, oxides, hydroxides, oxyhydroxides, and organic matter. Ion exchange reactions of lead on a number of clay minerals such as montmorillonite, kaolinite, illite, and vermiculite have been studied by a number of investigators. These studies showed that lead was preferentially adsorbed by exchange on clays, readily replacing calcium and potassium (Bittel and Miller, 1974; Overstreet and Krishnamurthy, 1950). Studies conducted by Lagerwerff and Brower (1973) on montmorillonitic, illitic, and kaolinitic soils confirmed that lead would preferentially exchange for calcium. Another clay mineral, vermiculite, is also known to exhibit very high ion exchange selectivity for lead (Rickard and Nriagu, 1978). Based on a number of studies Rickard and Nriagu (1978) also concluded that beyond neutral pH, precipitation reactions may control lead concentrations in solution rather than ion exchange and adsorption reactions involving clay mineral surfaces.

Experimental data show that only hydrogen ions and unhydrolyzed aluminum ions are capable of displacing lead from exchange sites on clay minerals (Lagerwerff and Brower, 1974; Zimdahl and Hassett, 1977). Clay minerals also differ in their exchange preference for lead. Bittel and Miller (1974) showed that the exchange preference for lead varies in the sequence,

kaolinite > illite > montmorillonite.

These studies also showed that, in neutral to high pH conditions, lead can preferentially exchange for calcium, potassium, and cadmium. Under low pH conditions, hydrogen ions and aluminum ions would displace lead from mineral exchange sites.

Studies of lead adsorption on oxide, hydroxide, and oxyhydroxide minerals show that the substrate properties, such as the specific surface and degree of crystallinity, control the degree of adsorption (Rickard and Nriagu, 1978). Experimental data by Forbes *et al.* (1976) showed that goethite (FeOOH) has higher adsorption affinity for lead than zinc, cobalt, and cadmium. Data show that manganese-oxide minerals also adsorb lead ions (Rickard and Nriagu, 1978). These investigators concluded that the high specificity of lead adsorption on oxide and hydroxide surfaces and the relative lack of desorbability (<10 percent) of adsorbed lead indicated that lead upon adsorption forms solid solutions with oxide or hydroxide surfaces. Therefore, this lack of reversibility indicated that the reaction is not a true adsorption phenomenon.

A number of studies have confirmed that many natural and synthetic organic materials adsorb lead. Data showing significant correlations between concentrations of organic matter and lead in soils indicate that soil organic matter has a higher affinity for lead adsorption as compared soil minerals.

A number of lead adsorption studies on bulk soils indicate that the adsorption is strongly correlated with pH and the CEC values of soils (Zimdahl and Hassett, 1977). A multiple regression analysis by Hassett (1974) of lead adsorption data indicated that properties that affect CEC of soils, such as organic matter content, clay content, and surface area, have a greater effect on lead adsorption than soil pH. The results of a number of studies of lead adsorption on a variety of soil and mineral surfaces were summarized by McLean and Bledsoe (1992). These data show that lead has very strong adsorption affinity as compared to a number of first row transition metals (cobalt, nickel, copper, and zinc). According to a recent study (Peters and Shem, 1992), the presence of very strong chelating organic ligands dissolved in solution will reduce adsorption of lead onto soils. These data show that the adsorption of lead in the environment is influenced by a number of factors such as the type and properties of adsorbing substrate, pH, the concentrations of lead, and the type and concentrations of other competing cations and complex forming inorganic and organic ligands.

### ***5.5.6 Partition Coefficient, $K_d$ , Values***

#### ***5.5.6.1 General Availability of $K_d$ Data***

The review of lead  $K_d$  data reported in the literature for a number of soils (Appendix F) led to the following important conclusions regarding the factors which influence lead adsorption on minerals and soils.<sup>1</sup> These principles were used to evaluate available quantitative data and generate a look-up table. These conclusions are:

- Lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated  $K_d$  values may reflect precipitation reactions rather than adsorption reactions.
- Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation.

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<sup>1</sup> Since the completion of our review and analysis of  $K_d$  data for the selected contaminants and radionuclides, the studies by Azizian and Nelson (1998) and Yong and MacDonald (1998) were identified and may be of interest to the reader.

- ~ A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases (as does precipitation) with increasing pH.
- ~ Adsorption of lead increases with increasing organic matter content of soils.
- ~ Increasing equilibrium solution concentrations correlates with decreasing lead adsorption (decrease in  $K_d$ ).

The factors which influence lead adsorption were identified from the following sources of data. A description and assessment of these data are provided in Appendix F. Lead adsorption behavior on soils and soil constituents (clays, oxides, hydroxides, oxyhydroxides, and organic matter) has been studied extensively. However, calculations by Rickard and Nriagu (1978) show that the solution lead concentrations used in a number of adsorption studies may be high enough to induce precipitation. For instance, their calculations show that lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated  $K_d$  values may reflect precipitation reactions rather than adsorption reactions.

Lead adsorption studies on manganese and iron oxides and oxyhydroxides indicate irreversible adsorption which was attributed to the formation of solid solution phases (*i.e.*, coprecipitation) (Forbes *et al.*, 1976; Grasselly and Hetenyi, 1971; Rickard and Nriagu, 1978). No correlations however have been established between the type and content of oxides in soil and the lead adsorption characteristics of soil.

Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation (Rickard and Nriagu, 1978). Presence of synthetic chelating ligands, such as EDTA, has been shown to reduce lead adsorption on soils (Peters and Shem, 1992). These investigators showed that the presence of strongly chelating EDTA in concentrations as low as 0.01 M reduced  $K_d$  for lead by about 3 orders of magnitude. By comparison quantitative data is lacking on the effects of more common inorganic ligands (phosphate, chloride, and carbonate) on lead adsorption on soils.

A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH (Braids *et al.*, 1972; Bittel and Miller, 1974; Griffin and Shimp, 1976; Haji-Djafari *et al.*, 1981; Hildebrand and Blum, 1974; Overstreet and Krishnamurthy, 1950; Scrudato and Estes, 1975; Zimdahl and Hassett, 1977). Griffin and Shimp (1976) also noted that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH values exceeded 5 or 6.

Solid organic matter such as humic material in soils is known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Correlative relationships between the organic matter content of soils and its effect on lead adsorption have been established by Gerritse *et al.* (1982) and Soldatini *et al.* (1976).

Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that  $K_d$  values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l).

#### 5.5.6.2 $K_d$ Look-Up Tables

Among all available data, Gerritse *et al.* (1982) obtained adsorption data at lead concentrations (0.0001 - 0.01 mg/l) which apparently precluded precipitation reactions. Also, these concentrations are within the range of lead concentrations most frequently encountered in ground waters (Chow, 1978). Additionally, data obtained by Rhoads *et al.* (1992) indicated that  $K_d$  values vary log-linearly as a function of equilibrium lead concentrations within the range of 0.00001 to 0.2 mg/l. The data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) were used to develop a look-up table (Table 5.9) of  $K_d$  as a function of soil pH and equilibrium lead concentrations.

##### 5.5.6.2.1 Limits of $K_d$ Values with Respect to pH

The pH ranges in the look-up table (Table 5.9) were selected from the rate of change that we noted in the  $K_d$  data as a function of pH. The  $K_d$  values within this pH range increase with increasing pH, and are greatest at the maximum pH limit (pH $\approx$ 11) of soils.

**Table 5.9.** Estimated range of  $K_d$  values for lead as a function of soil pH, and equilibrium lead concentrations.

| Equilibrium Lead Concentration (micro g/l) | $K_d$ (ml/g) | Soil pH   |           |            |
|--|--------------|-----------|-----------|------------|
|  |              | 4.0 - 6.3 | 6.4 - 8.7 | 8.8 - 11.0 |
| 0.1 - 0.9                                  | Minimum      | 940       | 4,360     | 11,520     |
|  | Maximum      | 8,650     | 23,270    | 44,580     |
| 1.0 - 9.9                                  | Minimum      | 420       | 1,950     | 5,160      |
|  | Maximum      | 4,000     | 10,760    | 20,620     |
| 10 - 99.9                                  | Minimum      | 190       | 900       | 2,380      |

|           |         |       |       |       |
|-----------|---------|-------|-------|-------|
|           | Maximum | 1,850 | 4,970 | 9,530 |
| 100 - 200 | Minimum | 150   | 710   | 1,880 |
|           | Maximum | 860   | 2,300 | 4,410 |

#### 5.5.6.2.2 Limits of $K_d$ Values with Respect to Equilibrium Lead Concentrations

The limits of equilibrium lead concentrations (0.0001 mg/l to about 0.2 mg/l) were selected based on the experimental data generated by Gerritse *et al.* (1982) and Rhoads *et al.* (1992). These investigators showed that within the range of initial lead concentrations used in their experiments the principal lead removal reaction from solution was adsorption and not precipitation. Four concentration ranges were selected to develop the  $K_d$  values.

### 5.6 Plutonium Geochemistry and $K_d$ Values

#### 5.6.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

In the ranges of pH and conditions typically encountered in the environment, plutonium can exist in all 4 oxidation states, namely +3, 4, +5, and +6. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist. Dissolved plutonium forms very strong hydroxy-carbonate mixed ligand complexes, therefore, its adsorption and mobility is strongly affected by these complex species. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes may be control adsorption and mobility of plutonium in the environment.

If plutonium is present as a distinct solid phase (amorphous or partly crystalline  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ ) or as a solid solution, the upper limits of aqueous plutonium concentrations would be in the  $10^{-12}$  to  $10^{-9}$  M range. Dissolved plutonium in the environment is typically present at  $\leq 10^{-15}$  M levels indicating that adsorption may be the principal phenomenon that regulates the mobility of this actinide.

Plutonium can adsorb on geologic material from low to extremely high affinities with  $K_d$  values ranging from 11 to 300,000 ml/g. Plutonium in the higher oxidation state adsorbed on iron oxide surfaces may be reduced to the tetravalent state by Fe(II) present in the iron oxides.

Two factors that influence the mobilization of adsorbed plutonium under environmental pH conditions (>7) are the concentrations of dissolved carbonate and hydroxyl ions. Both these ligands form very strong mixed ligand complexes with plutonium, resulting in desorption and increased mobility in the environment.

#### 5.6.2 General Geochemistry

Plutonium is produced by fissioning uranium fuel and is used in the construction of nuclear weapons. Plutonium has entered the environment either through accidental releases or through disposal of wastes generated during fuel processing and the production and detonation of nuclear weapons. Plutonium has 15 isotopes, but only 4 of these isotopes namely,  $^{238}\text{Pu}$  [ $t_{1/2}$  (half life) = 86 y],  $^{239}\text{Pu}$  ( $t_{1/2}$  = 24,400 y),  $^{240}\text{Pu}$  ( $t_{1/2}$  = 6,580 y),  $^{241}\text{Pu}$  ( $t_{1/2}$  = 13.2 y), are of environmental concern due to their abundances and long-half lives.

In the range of pH and redox conditions typically encountered in the environment, plutonium can exist in 4 oxidation states, namely +3, +4, +5, and +6 (Allard and Rydberg, 1983). Plutonium oxidation states are influenced by factors such as pH, presence of complexants and reductants, radiolysis, and temperature (Choppin, 1983). Observations indicate that under very low plutonium concentrations and oxidizing environmental conditions, the disproportionation<sup>1</sup> reactions of plutonium are not significant (Cleveland, 1979). Under reducing conditions, Pu(III) species would be dominant up to pH values approaching about 8.5, beyond which the Pu(IV) species are known to be the dominant species. However, under oxidizing conditions and at pH values greater than 4.0, plutonium can exist in +4,+5, and +6 oxidation states (Keeney-Kennicutt and Morse, 1985). A number of investigators believe that under oxidizing conditions, the +5 state to be the dominant redox state (Aston, 1980; Bondietti and Trabalka, 1980; Nelson and Orlandini, 1979; Rai *et al.*, 1980b).

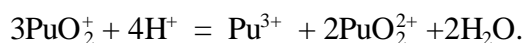
Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ , and/or  $^{240}\text{Pu}$  has been identified at 9 of the 45 Superfund National Priorities List (NPL) sites. The reported contamination includes airborne particulates, plutonium-containing soils, and plutonium dissolved in surface- and groundwaters.

### 5.6.3 Aqueous Speciation

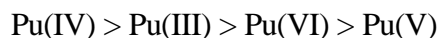
Dissolved plutonium forms complexes with various inorganic ligands such as hydroxyl, carbonate, nitrate, sulfate, phosphate, chloride, bromide, and fluoride; with many naturally occurring organic ligands such as acetate, citrate, formate, fulvate, humate, lactate, oxalate, and tartrate; and with

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<sup>1</sup> Disproportionation is a chemical reaction in which a single compound serves as both oxidizing and reducing agent and is thereby converted into more oxidized and a more reduced derivatives (Sax and Lewis, 1987). For the reaction to occur, conditions in the system must be temporarily changed to favor this reaction (specifically, the primary energy barrier to the reaction must be lowered). This is accomplished by a number of ways, such as adding heat or microbes, or by radiolysis occurring. Examples of plutonium disproportionation reactions are:



synthetic organic ligands such as EDTA and 8-hydroxyquinoline derivatives (Cleveland, 1979). Plutonium(IV) hydrolyzes more readily than all other redox species of plutonium (Baes and Mesmer, 1976). The order of hydrolysis of plutonium redox species follows the sequence



(Choppin, 1983). Plutonium hydrolytic species may have up to 4 coordinated hydroxyls. The tendency of plutonium in various oxidation states to form complexes depends on the ionic potential defined as the ratio ( $z/r$ ) of the formal charge ( $z$ ) to the ionic radius ( $r$ ) of an ion. Among plutonium redox species, Pu(IV) exhibits the highest ionic potential and therefore forms the strongest complexes with various ligands. Based on the equilibrium constants ( $K''_{r,298}$ ) for the plutonium complexation reactions, ligands, such as chloride and nitrate, form weak complexes ( $\log K''_{r,298}$  of 1 to 2) with plutonium, whereas fluoride, sulfate, phosphate, citrate, and oxalate form stronger complexes ( $\log K''_{r,298}$  of 6 to 30). Among the strongest complexes of plutonium are the hydroxy-carbonate mixed ligand complexes [*e.g.*,  $\text{Pu(OH)}_2(\text{CO}_3)_2^{2-}$ ] (Tait *et al.*, 1995; Yamaguchi *et al.*, 1994). Additionally, dissolved organic matter (fulvic and humic material) may also form complexes with plutonium. Although the nature of these complexes and their stability constants have not been fully characterized, it is believed that humic complexes of plutonium may be the dominant soluble species in natural environments at lower pH (below 5 to 6) values (Allard and Rydberg, 1983).

Because dissolved plutonium can exist in multiple redox states and form hydrolytic and complex species in solution, it is useful to assess the probable dominant plutonium aqueous species that may exist in typical ground water. Therefore, the aqueous speciation of dissolved plutonium was calculated as a function of pH using the MINTEQA2 code and a concentration of  $3.2 \times 10^{-10}$  mg/l ( $1.36 \times 10^{-15}$  M) total dissolved plutonium. This concentration is based on the maximum activity of  $^{239,240}\text{Pu}$  measured by Simpson *et al.* (1984) in 33 water samples taken from the highly alkaline Mono Lake in California. The species distribution was calculated assuming that multiple plutonium valence states might be present based on thermodynamic equilibrium considerations. This calculation is dependent on redox conditions as well as the pH and composition of the water. Therefore, a set of oxic conditions that might be associated with surface or near-surface disposal facilities or contaminated sites were selected for these illustrative calculations. These redox conditions are based on an experimentally determined pH/Eh relationship described in Lindsay (1979) for suspensions of sandy loam and distilled water. In a series of acid and base titrations, the pH/Eh response of the soil/water suspension was determined to vary according to the equation

$$\text{pe} + \text{pH} = 15.23 \quad (5.1)$$

where  $\text{pe}$  = negative log of the electron activity.<sup>1</sup>

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<sup>1</sup> The electron activity is defined as unity for the standard hydrogen electrode.

The pe is related to Eh by the equation

$$pe = (2.303RT/F) pe \quad (5.2)$$

where R = universal gas constant (1.9872 cal/mol·K)

T = temperature in degrees kelvin

F = Faraday constant (96,487 coulombs/equivalent).

At 25.0°C (298 K),

$$Eh(mV) = 5.92 pe \quad (5.3)$$

Using Equations 5.1 and 5.3, an Eh value was calculated for each pH value used as an input for the MINTEQA2 calculations of plutonium aqueous speciation. The plutonium aqueous species that were included in the computation scheme are tabulated in Table 5.10. Thermodynamic data for these species were taken primarily from Lemire and Tremaine (1980) and other secondary sources and database modifications described by Krupka and Serne (1996).

Results are plotted as a species distribution diagram (Figure 5.3). The data show that, under very low pH (~3 - 3.5) conditions,  $PuF_2^{2+}$  and  $PuO_2^+$  are the dominant species of plutonium. The free ionic species,  $PuO_2^+$  appears to be the dominant form within the pH range of 4 to 5. Within the pH range of 5.5 to 6.5, the main species of plutonium appear to be  $PuO_2^+$  and  $Pu(OH)_2(CO_3)_2^{2-}$ , with minor species being the neutral hydrolytic species  $Pu(OH)_4^{0}(aq)$  and the phosphate complex  $Pu(HPO_4)_4^{4-}$ . At pH values exceeding 6.5, the bulk of the dissolved plutonium (~90 percent) would be comprised of the  $Pu(OH)_2(CO_3)_2^{2-}$  species with a minor percentage of  $Pu(OH)_4^{0}(aq)$ . These illustrative computations indicate that, under pH conditions that typically exist in surface and groundwaters (>6.5), the dominant form of dissolved plutonium would be the tetravalent complex species,  $Pu(OH)_2(CO_3)_2^{2-}$ .

Polymeric species of plutonium may not occur under environmental conditions because the total plutonium concentrations in nature are at least 7 orders of magnitude less than the concentrations required for the formation of such species (Choppin, 1983). It is important to note that the speciation of plutonium would change significantly with changing redox conditions, pH, the types and total concentrations of complexing ligands and major cationic constituents.

#### **5.6.4 Dissolution/Precipitation/Coprecipitation**

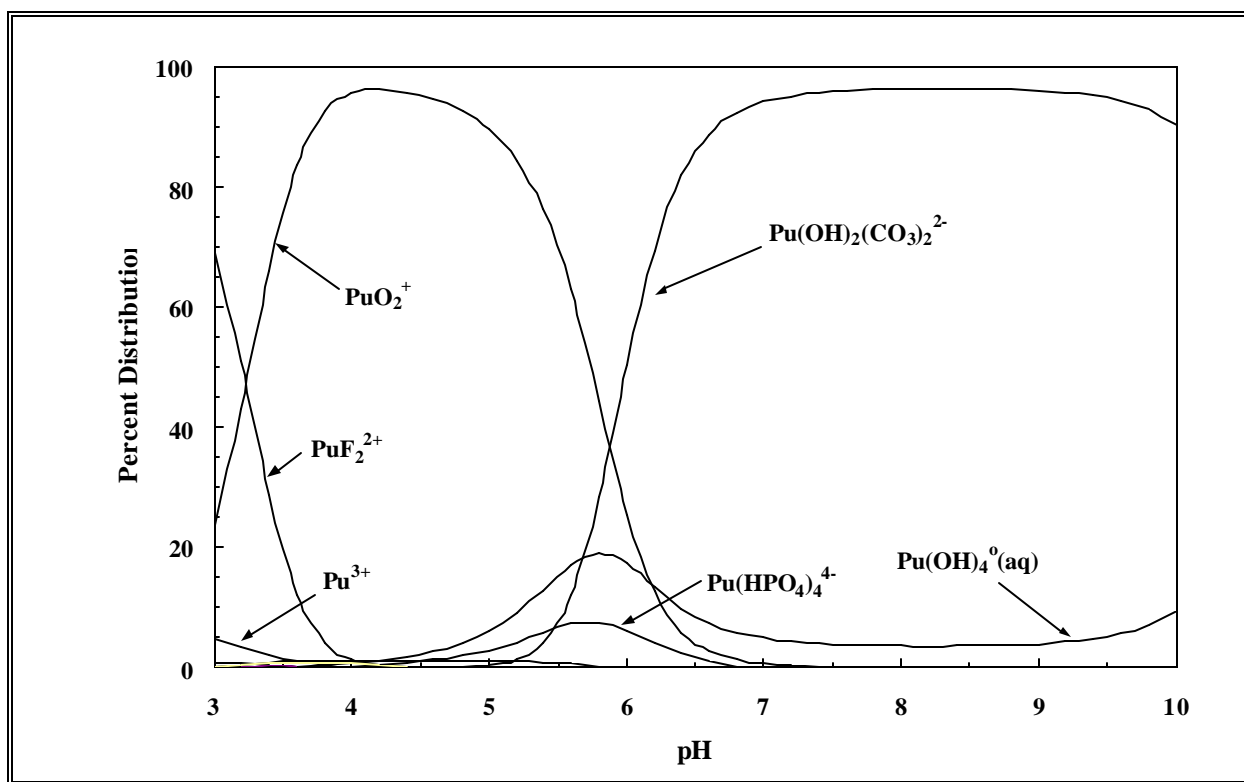
Allard and Rydberg (1983) calculated that the aqueous concentrations of plutonium in nature may be controlled by the solubility of the solid phase  $PuO_2 \cdot xH_2O$ . Many observations show that plutonium associated with soils and particulate organic matter is present in tetravalent oxidation state (Nelson and Lovett, 1980; Nelson *et al.*, 1987; Silver, 1983). Calculations by Allard and Rydberg (1983) based on available thermodynamic data show that, under reducing conditions, the solubility of dissolved



plutonium would be limited by the solid phase  $\text{PuO}_2$  at pH values greater than 8, and by the solid phase  $\text{Pu}_2(\text{CO}_3)_3$  of trivalent plutonium at lower pH values.

**Table 5.10.** Plutonium aqueous species included in the speciation calculations.

| Redox State | Aqueous Species   |
|-------------|---|
| Pu(III)     | $\text{Pu}^{3+}$ , $\text{PuOH}^{2+}$ , $\text{Pu}(\text{OH})_2^+$ , $\text{Pu}(\text{OH})_3^0(\text{aq})$<br>$\text{PuCO}_3^+$ , $\text{Pu}(\text{CO}_3)_2^-$ , $\text{Pu}(\text{CO}_3)_3^{3-}$<br>$\text{PuSO}_4^+$ , $\text{Pu}(\text{SO}_4)_2^-$<br>$\text{PuH}_2\text{PO}_4^{2+}$ , $\text{PuCl}^{2+}$   |
| Pu(IV)      | $\text{Pu}^{4+}$ , $\text{PuOH}^{3+}$ , $\text{Pu}(\text{OH})_2^{2+}$ , $\text{Pu}(\text{OH})_3^+$ , $\text{Pu}(\text{OH})_4^0(\text{aq})$<br>$\text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$ , $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$<br>$\text{PuSO}_4^{2+}$ , $\text{Pu}(\text{SO}_4)_2^0(\text{aq})$ , $\text{PuHPO}_4^{2+}$ , $\text{Pu}(\text{HPO}_4)_2^0(\text{aq})$ ,<br>$\text{Pu}(\text{HPO}_4)_3^{2-}$ , $\text{Pu}(\text{HPO}_4)_4^{4-}$<br>$\text{PuCl}^{3+}$ , $\text{PuF}^{3+}$ , $\text{PuF}_2^{2+}$ , $\text{PuF}_3^+$ , $\text{PuF}_4^0(\text{aq})$    |
| Pu(V)       | $\text{PuO}_2^+$ , $\text{PuO}_2\text{OH}^0(\text{aq})$ , $(\text{PuO}_2)_2\text{OH}^+$   |
| Pu(VI)      | $\text{PuO}_2^{2+}$ , $\text{PuO}_2\text{OH}^+$ , $\text{PuO}_2(\text{OH})_2^0(\text{aq})$ ,<br>$\text{PuO}_2(\text{OH})_3^-$ , $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ , $(\text{PuO}_2)_3(\text{OH})_5^+$<br>$\text{PuO}_2\text{CO}_3^0(\text{aq})$ , $\text{PuO}_2(\text{CO}_3)_2^{2-}$ , $\text{PuO}_2(\text{CO}_3)_3^{4-}$<br>$\text{PuO}_2\text{Cl}^+$ , $\text{PuO}_2\text{F}^+$ , $\text{PuO}_2\text{F}_2^0(\text{aq})$ , $\text{PuO}_2\text{F}_3^-$ , $\text{PuO}_2\text{F}_4^{2-}$<br>$\text{PuO}_2\text{SO}_4^0(\text{aq})$ , $\text{PuO}_2\text{H}_2\text{PO}_4^+$ |



**Figure 5.3.** Calculated distribution of plutonium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of  $3.2 \times 10^{-10}$  mg/l ( $1.36 \times 10^{-15}$  M) total dissolved plutonium.]

Laboratory studies conducted by Rai *et al.* (1980a), Delegard (1987), and Yamaguchi *et al.* (1994) indicated that a freshly precipitated amorphous  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  phase controls the equilibrium solubility of plutonium. Solubility on aged precipitates by Rai *et al.* (1980a) and Delegard (1987) also showed that equilibrium plutonium concentrations would be controlled by a partially crystallized  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  phase at concentrations about 2 orders of magnitude less than that of amorphous  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ . Therefore, under oxidizing conditions, amorphous  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ , if present in soils, may control soluble plutonium concentrations near  $10^{-8}$  M. Under alkaline conditions with high dissolved carbonate concentrations, dissolved plutonium concentrations may increase to micromolar levels. When dissolved carbonate is not present,  $\text{PuO}_2 \cdot x\text{H}_2\text{O}$  may control plutonium concentrations at about  $10^{-10}$  M (Rai *et al.*, 1980a).

### 5.6.5 Sorption/Desorption

Plutonium is known to adsorb onto soil components such as clays, oxides, hydroxides, oxyhydroxides, aluminosilicates and organic matter. Depending on the properties of the substrate, pH, and the composition of solution, plutonium would adsorb with affinities varying from low ( $K_d = 11$  ml/g) to extremely high ( $K_d = 300,000$  ml/g) (Baes and Sharp, 1983; Coughtrey *et al.*, 1985; Thibault *et al.*, 1990).

A number of studies indicate that iron hydroxides adsorb and reduce penta- and hexavalent plutonium to its tetravalent state at the solid surface. Experimental data showed that tetra- and pentavalent plutonium aqueous species oxidize to hexavalent form upon adsorption onto manganese dioxide surfaces whereas, pentavalent plutonium adsorbed on goethite disproportionate into tetra and hexavalent forms (Keeney-Kennicutt and Morse, 1985). Subsequently, the hexavalent form of plutonium was observed to have been reduced to tetravalent state. Additionally, these reactions were found to occur faster under light conditions than under dark conditions suggesting photochemical catalysis of adsorbed plutonium redox change reactions.

Laboratory studies have indicated that increasing carbonate concentrations decreased adsorption of tetra- and pentavalent plutonium on goethite surfaces (Sanchez *et al.*, 1985). Phenomenon similar to the reduction and suppression of plutonium adsorption in the presence of carbonate ions have also been observed for other actinides which also form strong hydroxy-carbonate mixed ligand aqueous species. These data suggest that plutonium would be most mobile in high pH carbonate-rich groundwaters.

Some studies indicate that the mass of plutonium retarded by soil may not be easily desorbed from soil mineral components. For example, Bunzl *et al.* (1995) studied the association of  $^{239+240}\text{Pu}$  from global fallout with various soil components. They determined the fractions of plutonium present as readily exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual minerals. For soils at their study site in Germany, the results indicated that 30-40 y after deposition of the plutonium, the readily exchangeable fraction of plutonium was less than 1 percent. More than 57 percent of the plutonium was sorbed to organic matter and a considerable mass sorbed to the oxide and mineral fractions.

### 5.6.6 Partition Coefficient, $K_d$ , Values

#### 5.6.6.1 General Availability of $K_d$ Data

A number of studies have focused on the adsorption behavior of plutonium on minerals, soils, and other geological materials.<sup>1</sup> A review of data from diverse sources of literature indicated that  $K_d$  values for plutonium typically range over 4 orders of magnitude (Thibault *et al.*, 1990). Also, based on a review of these data, a number of factors which influence the adsorption behavior of plutonium have been identified. These factors and their effects on plutonium adsorption on soils were used as the basis for generating a look-up table. These factors are:

- ~ Typically, in many experiments, the oxidation state of plutonium in solution was not determined or controlled. Therefore it would be inappropriate to compare the  $K_d$  data obtained from different investigations.
- ~ In natural systems with organic carbon concentrations exceeding ~10 mg/kg, plutonium exists mainly in trivalent and tetravalent redox states. If initial plutonium concentrations exceed  $\sim 10^{-7}$  M, the measured  $K_d$  values would reflect mainly precipitation reactions and not adsorption reactions.
- ~ Adsorption data show that the presence of ligands influence plutonium adsorption onto soils. Increasing concentrations of ligands decrease plutonium adsorption.
- ~ If no complexing ligands are present plutonium adsorption increases with increasing pH (between 5.5 and 9.0).
- ~ Plutonium is known to adsorb onto soil components such as aluminum and iron oxides, hydroxides, oxyhydroxides, and clay minerals. However, the relationship between the amounts of these components in soils and the measured adsorption of plutonium has not been quantified.

The factors which influence plutonium adsorption were identified from the following sources of data. A description and assessment of these data are provided in Appendix G. Because plutonium in nature can exist in multiple oxidation states (III, IV, V, and VI), soil redox potential would influence the Pu redox state and its adsorption on soils. However, our literature review found no plutonium adsorption studies which included soil redox potential as a variable. Studies conducted by Nelson *et al.* (1987) and Choppin and Morse (1987) indicated that the oxidation state of dissolved plutonium under natural

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<sup>1</sup> Since the completion of our review and analysis of  $K_d$  data for the selected contaminants and radionuclides, the studies by Duff *et al.* (1999) and Fisher *et al.* (1999) were identified and may be of interest to the reader.

conditions depended on the colloidal organic carbon content in the system. Additionally, Nelson *et al* (1987) also showed that plutonium precipitation occurred if the solution concentration exceeded  $10^{-7}$  M.

Plutonium complexation by ligands, such as acetate (Nishita, 1978; Rhodes, 1957), oxalate (Bensen, 1960), and fulvate (Bondietti *et al.*, 1975), are known to reduce adsorption of plutonium. Studies of suspended particles from natural water systems also showed that increasing concentrations of dissolved organic carbon decreased plutonium adsorption (Nelson *et al.*, 1987). Experiments using synthetic ligands such as EDTA (1 mmol/l), DTPA (1 mmol/l), and HEDTA (100 mmol/l) have shown that plutonium adsorption onto soils was reduced due to complexing effects of these ligands (Delegard *et al.*, 1984; Relyea and Brown, 1978). However, it is unlikely that such concentrations of these synthetic ligands would exist in soils. The effects of carbonate ions on Pu(IV) adsorption on goethite have been quantified by Sanchez *et al.* (1985). They found that carbonate concentrations exceeding 100 mmol/l significantly reduced adsorption of Pu(IV) on goethite. In contrast, under soil saturation extract conditions in which carbonate concentrations typically range from 0.1 to 6 mmol/l  $\text{HCO}_3^-$ , Pu(IV) adsorption appears to increase with increasing carbonate concentration (Glover *et al.*, 1976).

Rhodes (1957) and Prout (1958) conducted studies of plutonium adsorption as a function of pH. Both these studies indicated that Pu exhibited an adsorption maxima between pH values 6.5 to 8.5. These data however are unreliable because initial plutonium concentrations of  $6.8 \times 10^{-7}$  to  $1 \times 10^{-6}$  M used in the experiments may have resulted in precipitation reactions thus confounding the observations.

Even though the adsorption behavior of plutonium on soil minerals such as glauconite (Evans, 1956), montmorillonite (Billon, 1982; Bondietti *et al.*, 1975), attapulgite (Billon, 1982), and oxides, hydroxides, and oxyhydroxides (Evans, 1956; Charyulu *et al.*, 1991; Sanchez *et al.*, 1985; Tamura, 1972; Ticknor, 1993; Van Dalen *et al.*, 1975) has been studied, correlative relationships between the type and quantities of soil minerals in soils and the overall plutonium adsorption behavior of the soils have not been established.

Plutonium adsorption data for 14 soils have been collected by Glover *et al.* (1976) along with a number of soil properties that included soil organic matter content. A multiple regression analyses of these data showed that compared to other soil parameters such as clay mineral content, dissolved carbonate concentration, electrical conductivity and pH, soil organic matter was not a significant variable.

These criteria were used to evaluate and select plutonium adsorption data in developing a look-up table. Only 2 adsorption studies using soils in which the initial concentrations of Pu(IV) used were less than the concentration that would trigger precipitation reactions. Barney (1984) conducted adsorption experiments in which initial plutonium concentrations of  $10^{-11}$  to  $10^{-9}$  M were used to examine plutonium adsorption on to basalt interbed sediments from Hanford, Washington. Glover *et al.* (1976) conducted a set of experiments using  $10^{-8}$  M initial concentration to study the adsorption behavior of Pu(IV) on

14 different soil samples from 7 DOE sites. A number of soil properties were also measured thus providing a basis to correlate the adsorption behavior with a number of soil parameters. This is the best available data set for Pu(IV) adsorption on a number of well characterized soils therefore, it was used to develop correlative relationships and a look-up table for  $K_d$  values.

#### 5.6.6.2 $K_d$ Look-Up Table

The look-up table for plutonium  $K_d$  values (Table 5.11) was generated using the a piece-wise regression model with clay content and dissolved carbonate as the independent variables (See Appendix G for details).

##### 5.6.6.2.1 Limits of $K_d$ Values with Respect to Clay Content

The clay contents of the soils used for developing the regression relationship ranged from 3 to 64 percent by weight. Therefore the range of clay contents for the look-up table was set between 0 and 70 percent. Extending the regression relationship for high clay soils (>70 percent) would result in a higher degree of uncertainty for predicted  $K_d$  values. Clay contents of soils are typically measured as part of textural analysis of soil. Clay content of a soil is defined as the mass of soil particles with average particle size of  $\leq 2$  micro m.

**Table 5.11.** Estimated range of  $K_d$  values for plutonium as a function of the soluble carbonate and soil clay content values.

| $K_d$ (ml/g) | Clay Content (wt.%)          |       |       |                              |       |       |                              |       |       |
|--------------|------------------------------|-------|-------|------------------------------|-------|-------|------------------------------|-------|-------|
|              | 0 - 30                       |       |       | 31 - 50                      |       |       | 51 - 70                      |       |       |
|              | Soluble Carbonate<br>(meq/l) |       |       | Soluble Carbonate<br>(meq/l) |       |       | Soluble Carbonate<br>(meq/l) |       |       |
|              | 0.1 - 2                      | 3 - 4 | 5 - 6 | 0.1 - 2                      | 3 - 4 | 5 - 6 | 0.1 - 2                      | 3 - 4 | 5 - 6 |
| Minimum      | 5                            | 80    | 130   | 380                          | 1,440 | 2,010 | 620                          | 1,860 | 2,440 |
| Maximum      | 420                          | 470   | 520   | 1,560                        | 2,130 | 2,700 | 1,980                        | 2,550 | 3,130 |

#### 5.6.6.2.2 Limits of $K_d$ Values with Respect to Dissolved Carbonate Concentrations

The dissolved carbonate content of the soils used for the regression relationships ranged from about 0.1 to 6 meq/l (0.1 to 6 mmol/l of  $\text{HCO}_3^-$ ). The dissolved carbonate values were measured on saturation extracts obtained from these soils. The standard procedure for obtaining saturation extracts from soils has been described by Rhoades (1996). The saturation extracts are obtained by saturating and equilibrating the soil with distilled water followed by vacuum filtration to collect the extract. Saturation extracts are usually used to determine the pH, the electrical conductivity, and dissolved salts in soils. For soils with pH values less than 8.5, the saturation extracts typically contain less than 8 mmol/l of dissolved carbonate (Richards, 1954).

The regression relationship indicates that within the range of 0.1 to 6 mmol/l of dissolved carbonate, the  $K_d$  values increase with increasing dissolved carbonate values. Adsorption experiments conducted by Sanchez *et al.* (1985) showed however that very high concentrations (100 to 1,000 meq/l) of dissolved carbonate in matrix solution decreases Pu adsorption on goethite. The dissolved carbonates in soil saturation extracts are 3 to 4 orders of magnitude less than the concentrations used in experiments by Sanchez *et al.* (1985). The data by Glover *et al.* (1976) show that within very low concentration range of dissolved carbonate (0.1 to 6 mmol/l) found soil saturation extracts,  $K_d$  values for Pu increase as a function of dissolved carbonate. This correlation may be strictly serendipitous and a more likely variable that would lead to an increased  $K_d$  would be increasing pH.

### 5.7 Radon Geochemistry and $K_d$ Values

#### 5.7.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

The migration of radon, an inert gas, in soil/water systems is not affected itself by aqueous speciation, precipitation/dissolution, or adsorption/desorption processes. Therefore, the mobility of radon is not affected by issues associated with the selection of appropriate “adsorption”  $K_d$  values for modeling contaminant transport and risks in soil /water systems. Radon is soluble in water, and the hydrostatic pressure on ground water below the water table is sufficient to keep dissolved radon in solution.

The generation of radon is however affected by the concentrations of its parent elements which, along with radon’s decay products, are of regulatory concern. Because aqueous speciation, precipitation/dissolution, or adsorption/desorption processes can affect the movement of radon’s parents and decay products in soils, these processes should be considered when modeling contaminant transport in a total environmental system, including air transport pathways.



### 5.7.2 General Geochemistry

Radon is a colorless, odorless, essentially inert gas. All radon isotopes are radioactive. The longest-lived isotope of radon is  $^{222}\text{Rn}$  which has a half life ( $t_{1/2}$ ) of 3.8 d. The main health risk is from inhalation of radon gas and its daughter products which are usually adsorbed on dust in the air. Detailed descriptions of the geologic controls, migration, and detection of radon have been included in published proceedings such as Graves (1987), Gesell and Lowder (1980), and elsewhere. Of the 45 Superfund National Priorities List (NPL) sites considered in EPA/DOE/NRC (1993), radioactive contamination of air, soil, surface water, and/or groundwater by  $^{220}\text{Rn}$  and/or  $^{222}\text{Rn}$  has been identified at 23 sites.

Twenty isotopes of radon are known (Weast and Astle, 1980). Environmental radon contamination typically results from radioactive decay of isotopes in the uranium-thorium series. These include the formation of:

- $^{222}\text{Rn}$  by alpha decay from  $^{226}\text{Ra}$  in the  $^{238}\text{U}$  decay series
- $^{220}\text{Rn}$  ( $t_{1/2}=54$  sec) by alpha decay from  $^{224}\text{Ra}$  in the  $^{232}\text{Th}$  decay series
- $^{219}\text{Rn}$  ( $t_{1/2}=3.9$  sec) by alpha decay from  $^{223}\text{Ra}$  in the  $^{238}\text{U}$  decay series.

The final, stable daughter products in these 3 decay series are  $^{206}\text{Pb}$ ,  $^{208}\text{Pb}$ , and  $^{207}\text{Pb}$ , respectively.

Some noble gases (*i.e.*, krypton, xenon, and radon) have very limited chemical reactivity with other elements. The chemical reactivity of radon is difficult to assess because of its short half life.

Geologic and hydrogeologic processes that might influence radon mobility are discussed in detail by Tanner (1980). As an inert gas, radon is not immobilized by precipitation processes along migration pathways. According to data cited by Tanner (1980), the ratio (*i.e.*, solubility distribution coefficient) of  $^{222}\text{Rn}$  in a water phase to that in a gas phase ranges from 0.52 at 0°C to 0.16 at 40°C. This ratio has been used, for example, for the solubility of radon in water in mathematical models designed to calculate radon diffusion coefficients in soils (*e.g.*, Nielson *et al.*, 1984). The solubility of radon in organic liquids is greater than that in water.

### 5.7.3 Aqueous Speciation

The existence of radon aqueous species was not identified in any of the references reviewed for this study. Given the inertness of radon and the short half life ( $t_{1/2}=3.8$  d) for  $^{222}\text{Rn}$ , aqueous speciation and complexation of dissolved radon would not be expected to be important.

However, as noted above, radon is soluble in water. The hydrostatic pressure on ground water below the water table is sufficient to keep dissolved radon in solution. Above the water table, the radon

present in vadose zone pore water will exsolve from solution, enter the vapor phase, and migrate as part of the air through the open rock and soil pore spaces.

#### ***5.7.4 Dissolution/Precipitation/Coprecipitation***

Because radon exists as a dissolved gas, dissolution/precipitation processes are not important relative to the geochemical behavior of radon and its movement through aqueous environments. These processes are, however, important relative to the geochemical behavior of radon's parent elements (*e.g.*, radium) and associated mechanisms by which the radon gas escapes from the solid phases into ground- and soil waters.

Rama and Moore (1984) studied the mechanism for the release of  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  from solid aquifer material. They determined that radon and other decay products from the U-Th series were released by alpha recoil<sup>1</sup> from the walls of nanometer-size pores in the aquifer solids. Radon diffused into the intergranular water for release to the atmosphere or decay to more long-lived products. These decay products may in turn diffuse from the intergranular water and become adsorbed onto the walls of the nanometer-size pores.

#### ***5.7.5 Adsorption/Desorption***

Adsorption processes are not expected to be important relative to the geochemical behavior of gaseous radon and its movement through aqueous environments. The lack of importance of sorption processes is also supported by studies conducted at cryogenic temperatures (Tanner, 1980). However, as noted by Tanner (1980), "adsorption effects on the release of radon isotopes from geologic materials have not been studied sufficiently to determine unambiguously whether they are an important factor."

#### ***5.7.6 Partition Coefficient, $K_d$ , Values***

Because adsorption processes are not important relative to the movement of gaseous radon through aqueous environments, a review of  $K_d$  values for radon was not conducted. Compilations, such as Thibault *et al.* (1990), do not list any  $K_d$  values for radon. A  $K_d$  value of zero should be considered for radon.

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<sup>1</sup> Alpha recoil refers to the displacement of an atom from its structural position, as in a mineral, resulting from radioactive decay of the release an alpha particle from its parent isotope (*e.g.*, alpha decay of  $^{222}\text{Rn}$  from  $^{226}\text{Ra}$ ).

## 5.8 Strontium Geochemistry and $K_d$ Values

### 5.8.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Strontium in solution is expected to be predominantly present as the uncomplexed  $\text{Sr}^{2+}$  ion. Only in highly alkaline soils could strontianite ( $\text{SrCO}_3$ ) control strontium concentrations in solutions. The extent to which strontium partitions from the aqueous phase to the solid phase is expected to be controlled primarily by the CEC of the solid phase. In environments with a pH greater than 9 and dominated by carbonates, coprecipitation with  $\text{CaCO}_3$  and/or precipitation as  $\text{SrCO}_3$  may become an increasingly important mechanism controlling strontium removal from solution (Lefevre *et al.*, 1993). A direct correlation between solution pH and strontium  $K_d$  has been reported (Prout, 1958; Rhodes, 1957). This trend is likely the result of hydrogen ions competing with  $\text{Sr}^{2+}$  for exchange sites and the result of pH increasing the CEC. Strontium  $K_d$  values may decrease from 100 to 200 ml/g in low ionic strength solutions to less than 5 ml/g in high ionic strength solutions (Routson *et al.*, 1980). Calcium is an important competing cation affecting  $^{90}\text{Sr}$   $K_d$  values (Kokotov and Popova, 1962; Schulz, 1965). The most important ancillary parameters affecting strontium  $K_d$  values are CEC, pH, and concentrations of calcium and stable strontium.

### 5.8.2 General Geochemistry

Strontium exists in nature only in the +2 oxidation state. The ionic radius of  $\text{Sr}^{2+}$  is 1.12 Å, very close to that of  $\text{Ca}^{2+}$  at 0.99 Å (Faure and Powell, 1972). As such, strontium can behave chemically as a calcium analog, substituting for calcium in the structure of a number of minerals. Strontium has 4 naturally occurring isotopes:  $^{84}\text{Sr}$  (0.55 percent),  $^{86}\text{Sr}$  (9.75 percent),  $^{87}\text{Sr}$  (6.96 percent), and  $^{88}\text{Sr}$  (82.74 percent). The other radioisotopes of strontium are between  $^{80}\text{Sr}$  and  $^{95}\text{Sr}$ . Only  $^{90}\text{Sr}$  [half life ( $t_{1/2}$ ) = 28.1 y], a fission product, is of concern in waste disposal operations and environmental contamination. The radionuclide  $^{89}\text{Sr}$  also is obtained in high yield, but the half-life is too short ( $t_{1/2}$  = 52 d) to create a persistent environmental or disposal problem. Because of atmospheric testing of nuclear weapons,  $^{90}\text{Sr}$  is distributed widely in nature. The average  $^{90}\text{Sr}$  activity in soils in the United States is approximately 100 mCi/mi<sup>2</sup>. As a calcium analog,  $^{90}\text{Sr}$  tends to accumulate in bone (UNSCEAR, 1982).

Contamination includes airborne particulates, strontium-containing soils and strontium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination by  $^{90}\text{Sr}$  has been identified at 11 of the 45 Superfund National Priorities List (NPL).

### 5.8.3 Aqueous Speciation

There is little tendency for strontium to form complexes with inorganic ligands (Faure and Powell, 1972). The solubility of the free  $\text{Sr}^{2+}$  ion is not greatly affected by the presence of most inorganic anions. Dissolved strontium forms only weak aqueous complexes with carbonate, sulfate, chloride, and nitrate. For example, Izrael and Rovinskii (1970) used electrodialysis to study the chemical state of strontium leached by groundwater from rubble produced in a nuclear explosion. They found that 100 percent of the strontium existed as uncomplexed  $\text{Sr}^{2+}$ , with no colloidal or anionic strontium present in the leachate. Stevenson and Fitch (1986) concluded that strontium should not form strong complexes with fulvic or humic acids based on the assumptions that strontium would exhibit similar stability with organic ligands as calcium and that strontium could not effectively compete with calcium for exchange sites because calcium would be present at much greater concentrations. Thus, organic and inorganic complexation is not likely to greatly affect strontium speciation in natural groundwaters.

Species distribution of strontium was calculated using the water composition described in Table 5.1 and a concentration of 0.11 mg/l total dissolved strontium. Hem (1985, p. 135) lists this value as a median concentration of dissolved strontium for larger United States public water supplies based on analyses from Skougstad and Horr (1963). The strontium aqueous species included in the speciation calculations are listed in Table 5.12. These MINTEQA2 calculations support the contention that strontium will exist in groundwaters predominantly as the uncomplexed  $\text{Sr}^{2+}$  ion. The  $\text{Sr}^{2+}$  ion dominates the strontium speciation throughout the pH range of 3 to 10. Between pH 3 and 8.5, the  $\text{Sr}^{2+}$  species constitutes approximately 98 percent of the total dissolved strontium. The remaining 2 percent is composed of the neutral species  $\text{SrSO}_4^0(\text{aq})$ . Between pH 9 and 10,  $\text{SrCO}_3^0(\text{aq})$  is calculated to be between 2 and 12 percent of the total dissolved strontium. As the pH increases above 9, the  $\text{SrCO}_3^0(\text{aq})$  complex becomes increasingly important. The species distribution for strontium does not change if the concentration of total dissolved cadmium is increased from 1 to 1,000 micro g/l.

#### ***5.8.4 Dissolution/Precipitation/Coprecipitation***

Strontium is an alkaline-earth element, which also includes beryllium, magnesium, calcium, strontium, barium and radium, and can form similar solid phases as calcium. For instance, the 2 most prevalent strontium minerals, celestite ( $\text{SrSO}_4$ ) and strontianite ( $\text{SrCO}_3$ ), have calcium counterparts, anhydrite ( $\text{CaSO}_4$ ), and calcite ( $\text{CaCO}_3$ ). In an acidic environment, most of the strontium solids will be highly soluble, and, if the activity of  $\text{Sr}^{2+}$  in solution exceeds approximately  $10^{-4}$  mol/l, celestite may precipitate to form a stable phase. However, in alkaline conditions, strontianite would be the stable solid phase and could control strontium concentrations in soil solutions. However, the dissolved strontium concentrations in most natural waters are generally well below the solubility limit of strontium-containing minerals.

**Table 5.12.** Strontium aqueous species included in the speciation calculations.

| Aqueous Species   |
|---|
| $\text{Sr}^{2+}$ , $\text{SrOH}^+$  |
| $\text{SrCO}_3^{\text{''}}(\text{aq})$ , $\text{SrSO}_4^{\text{''}}(\text{aq})$ , $\text{SrNO}_3^+$                       |
| $\text{SrCl}^+$ , $\text{SrF}^+$  |
| $\text{SrPO}_3^-$ , $\text{SrHPO}_4^{\text{''}}(\text{aq})$ , $\text{SrH}_2\text{PO}_4^+$ , $\text{SrP}_2\text{O}_7^{2-}$ |

Because strontium generally exists in nature at much lower concentration than calcium, it commonly does not form pure phases (Faure and Powell, 1972). Instead it forms coprecipitates (solid solutions) with calcite and anhydrite. Calcite can allow the substitution of several hundred parts per million strontium before there is any tendency for strontianite to form. Strontium can also coprecipitate with barium to form  $(\text{Ba}_{(1-x)}\text{Sr}_x)\text{SO}_4$  in more-alkaline environments (Ainsworth and Rai, 1987; Felmy *et al.*, 1993).

#### 5.8.5 Adsorption/Desorption

A great deal of research has been directed at understanding and measuring the extent to which strontium adsorbs to soils [reviewed by Ames and Rai (1978) and Streng and Peterson (1989)]. The primary motivation for this research is the need to understand the environmental fate and mobility of  $^{90}\text{Sr}$ , particularly as it relates to site remediation and risk assessment. The mechanism by which

strontium partitions from the dissolved phase to the solid phase at pH values less than 9 is commonly believed to be cation exchange<sup>1</sup> (Ames and Rai, 1978; Lefevre *et al.*, 1993; McHenry, 1958).

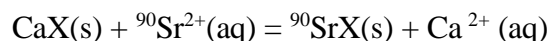
Among the most important environmental parameters affecting the magnitude of a strontium  $K_d$  value is the soil CEC (Ames and Rai, 1978; Lefevre *et al.*, 1993; McHenry, 1958). This finding is consistent with cation exchange proposed as the mechanism generally controlling strontium adsorption. The results of Serne and LeGore (1996) also indicate that strontium adsorption is largely controlled by cation exchange. They reported that  $^{90}\text{Sr}$  adsorption was reversible; that is, strontium could be easily desorbed (exchanged) from the surfaces of soils. Natural soils that had been in contact with  $^{90}\text{Sr}$  for approximate 27 y could be leached of adsorbed  $^{90}\text{Sr}$  as readily as similar soils containing recently adsorbed strontium, indicating that  $^{90}\text{Sr}$  does not become more recalcitrant to leaching with time. Furthermore, these studies suggested that cation exchange, and not (co)precipitation, was responsible for  $^{90}\text{Sr}$  sorption because the latter would leach at a much slower rate.

Some studies indicate that a fraction of some  $^{90}\text{Sr}$  sorbed to soil components may not be readily exchanged [see review in Brady *et al.* (1999)]. For example, Schulz and Riedel (1961) studied the influence of aging on the sorption of carrier-free  $^{90}\text{Sr}$  into nonexchangeable forms by three soils. They observed that less than 10% of the total applied carrier-free  $^{90}\text{Sr}$  was not easily exchanged which they attributed to adsorption onto solid-phase carbonates or phosphates. A study by Wiklander (1964) indicated that after 4 y, only 90 percent of the  $^{90}\text{Sr}$  added to the soil could be displaced by repeated acidic ammonium acetate (pH 4.6) extractions. Wiklander proposed that the retention of  $^{90}\text{Sr}$  was due to strontium substituting for calcium into or adsorbing onto calcium-bearing minerals. Studies by Roberts and Menzel (1961) and Taylor (1968) showed that as much as 50% of the  $^{90}\text{Sr}$  in some acidic soils was not readily exchangeable. In sediments sampled from the White Oak Creek watershed at DOE's Oak Ridge Site, Cerling and Spalding (1982) determined that the majority of the  $^{90}\text{Sr}$  present in the sediments was weakly adsorbed and exchangeable, but substantial mass was fixed in the sediments. They found that approximately 80-90 percent of  $^{90}\text{Sr}$  present in these sediments was extracted by warm 1N NaCl or  $\text{NH}_4\text{OAC}$  solutions and quantitative extraction required hot 8 N nitric acid.

Some important ancillary soil properties include the natural strontium and calcium concentrations in the aqueous and solid phases (Kokotov and Popova, 1962; Schulz, 1965), mineralogy (Ames and Rai,

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<sup>1</sup> Cation exchange is a reversible adsorption reaction in which an aqueous species exchanges with an adsorbed species. Cation exchange reactions are approximately stoichiometric and can be written, for example, as



where X designates an exchange surface site. Adsorption phenomena are discussed in more detail in Volume I of this report.

1978), pH (Juo and Barber, 1970; Prout, 1958; Rhodes, 1957), and solution ionic strength (Rhodes, 1957; Routson *et al.*, 1980). Numerous studies have been conducted to elucidate the effects of competing cations on strontium adsorption [reviewed by Ames and Rai (1978) and Streng and Peterson (1989)]. These experiments consistently show that, on an equivalence basis, strontium will dominate most Group 1A and 1B elements (alkaline and alkaline earth elements) in competition for exchange sites.

A ranking of the most common groundwater cations by their ability to displace strontium from an exchange site is:

$$\text{Stable Sr} > \text{Ca} > \text{Mg} > \text{K} \geq \text{NH}_4 > \text{Na} \quad (5.4)$$

(Kokotov and Popova, 1962). Calcium exists in groundwaters at concentrations typically 2 orders of magnitude greater than stable strontium and typically more than 12 orders of magnitude greater than  $^{90}\text{Sr}$  (Table 5.1). Consequently, mass action would improve the likelihood of calcium out competing  $^{90}\text{Sr}$  for exchange sites.

Rhodes (1957) showed the effect of solution pH and ionic strength on the adsorption of strontium on soils containing carbonate minerals and montmorillonite. The pH of the system was adjusted with NaOH or HCl and the ionic strength was adjusted by adding 4 M NaNO<sub>3</sub>. For a dilute solution, the strontium  $K_d$  increased from 5 ml/g at pH 6 to 10 ml/g at pH 8, and 120 ml/g at pH 10. Above pH 10, strontium adsorption began to level off, and the sodium added in the NaOH used for pH adjustment began to compete for exchange sites with the strontium. In 4 M NaNO<sub>3</sub> (an extremely high ionic strength solution with respect to natural environments), strontium adsorption was much less affected by pH. At pH 8, for example, the strontium  $K_d$  was about 5 ml/g and increased to about 10 ml/g at pH 10. Using kaolinitic soils from South Carolina, Prout (1958) reported very similar pH and ionic strength effects as Rhodes (1957). A maximum strontium adsorption was reached at about pH 10, although this maximum was much higher ( $K_d = 700$  to 800 ml/g) than that reported by Rhodes (1957). Prout (1958) also reported only a slight pH effect on strontium  $K_d$  values in high ionic strength solutions. Rhodes (1957) and Prout (1958) reported that increases in ionic strength resulted in lower strontium  $K_d$  values.

### **5.8.6 Partition Coefficient, $K_d$ , Values**

#### **5.8.6.1 General Availability of $K_d$ Data**

Two simplifying assumptions underlying the selection of strontium  $K_d$  values included in the look-up table were made. Strontium adsorption: (1) occurs by cation exchange, and (2) follows a linear isotherm. These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are compromised in systems with strontium concentration

greater than about  $10^{-4}$  M, humic substance concentration greater than about 5 mg/l, ionic strength levels greater than about 0.1 M, and pH levels greater than about 12.

Based on these assumptions and limitation, strontium  $K_d$  values and some important ancillary parameters that influence cation exchange were collected from the literature and tabulated (Appendix H).<sup>1</sup> Data included in this table, were from studies that reported  $K_d$  values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of (1) natural soils (as opposed to pure mineral phases), (2) low ionic strength ( $<0.1$  M), (3) pH values between 4 and 10, (4) strontium concentrations less than  $10^{-4}$  M, (5) low humic material concentrations ( $<5$  mg/l), and (6) no organic chelates (*e.g.*, as EDTA). Initially, attempts were made to include in the  $K_d$  data set all the key aqueous- and solid-phase parameters identified above. These parameters included CEC, pH, calcium concentration, stable strontium concentration, and carbonate concentration.

The ancillary parameters for which data could be found that was included in these tables were clay content, pH, CEC, surface area, solution calcium concentrations, and solution strontium concentrations. This table described 63 strontium  $K_d$  values. A second table containing strontium  $K_d$  values for soils as well as pure mineral phases was prepared at the same time and this table contained 166 entries. These data are included in Appendix H but were not used to provide guidance regarding the selection of  $K_d$  values to be included in the look-up table.

#### 5.8.6.2 Look-Up Table

The look-up table requires knowledge of the CEC (or clay content) and pH of the system in order to select the appropriate strontium  $K_d$  value (Table 5.13). A detailed explanation of the approach used in selecting these  $K_d$  values is presented in Appendix H. Briefly, it involves tabulating the  $K_d$  and ancillary data found in the literature and then conducting regression analysis of the data with strontium  $K_d$  as the dependent variable. Selection of independent variables used in the final look-up tables was based in part on their correlation coefficients. Perhaps more importantly, the independent variables had to be a parameter that is readily available to modelers. For instance, particle size and pH are often available to modelers whereas such parameters as iron oxide or surface area are not as frequently available. The estimated ranges for the minimum and maximum  $K_d$  values were based on regression estimates of the 95 percent error ( $P < 0.05$ ). The central estimates were based primarily on values calculated using the appropriate regression equations.

##### 5.8.6.2.1 Limits of $K_d$ Values with Respect to pH, CEC and Clay Content Values

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<sup>1</sup> Since the completion of our review and analysis of  $K_d$  data for the selected contaminants and radionuclides, the studies by Chen *et al.* (1998), Fisher *et al.* (1999), Oscarson and Hume (1998), and Wang *et al.* (1998) were identified and may be of interest to the reader.



A full factorial table was created that included 3 pH categories and 3 CEC categories, resulting in 9 cells (Table 5.13). Each cell contains an estimated minimum and maximum  $K_d$  value. As the pH or the CEC of a system increases, so does the strontium  $K_d$  values.

A second table was created based on Table 5.13, in which clay content replaced CEC as an independent variable (subset of Table 5.13). This second table was created because it is likely that clay content data will be more readily available for modelers than CEC data. To accomplish this, clay contents associated with the CEC values used to delineate the different categories were calculated using regression equations (see Appendix H). for additional details).

#### 5.8.6.2.2 Limits of $K_d$ Values with Respect to Dissolved Calcium Concentrations

Of the 63 experiments reporting strontium  $K_d$  values, 32 also reported dissolved calcium concentrations (Appendix H). The mean calcium concentration in this data set was 56 mg/l, with a minimum of 0 mg/l and a maximum of 400 mg/l. Calcium concentration had a correlation with strontium  $K_d$  values,  $r = -0.17$ . Although this correlation is insignificant, it does show that the relationship between these 2 parameters is negative. This inverse relationship can be attributed to calcium competing with strontium for adsorption sites on the solid phase.

**Table 5.13.** Look-up table for estimated range of  $K_d$  values for strontium based on CEC (meq/100 g), clay content (wt.%), and pH. [Tabulated values pertain to systems consisting of natural soils (as opposed to pure mineral phases), low ionic strength (< 0.1 M), low humic material concentrations (<5 mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

| $K_d$ (ml/g) | CEC (meq/100 g) / Clay Content (wt.%) |       |        |                 |       |        |                   |       |        |
|--------------|---------------------------------------|-------|--------|-----------------|-------|--------|-------------------|-------|--------|
|              | 3 / < 4                               |       |        | 3 - 10 / 4 - 20 |       |        | 10 - 50 / 20 - 60 |       |        |
|              | pH                                    |       |        | pH              |       |        | pH                |       |        |
|              | < 5                                   | 5 - 8 | 8 - 10 | < 5             | 5 - 8 | 8 - 10 | < 5               | 5 - 8 | 8 - 10 |
| Minimum      | 1                                     | 2     | 3      | 10              | 15    | 20     | 100               | 200   | 300    |
| Maximum      | 40                                    | 60    | 120    | 150             | 200   | 300    | 1,500             | 1,600 | 1,700  |

#### 5.8.6.2.3 Limits of $K_d$ Values with Respect to Dissolved Stable Strontium and Carbonate Concentrations

Of the 63 experiments reporting strontium  $K_d$  values, none reported stable strontium or carbonate concentrations (Appendix H). It was anticipated that the presence of stable strontium would compete with the  $^{90}\text{Sr}$  for exchange sites, thereby decreasing  $^{90}\text{Sr}$   $K_d$  values. The presence of dissolved carbonate would likely decrease  $^{90}\text{Sr}$   $K_d$  values due to formation of the weaker strontium-carbonate aqueous complex.

### 5.9 Thorium Geochemistry and $K_d$ Values

#### 5.9.1 Overview: Important Aqueous- and Solid-Phase Parameters Controlling Retardation

Thorium occurs only in the +4 oxidation state in nature. In aqueous solutions, especially in natural waters, the concentrations of dissolved thorium are very low. Dissolved thorium forms a variety of hydroxyl species, and undergoes extensive chemical interaction with water and most anions. Thorium can form various aqueous complexes with inorganic anions such as dissolved carbonate, fluoride, phosphate, chloride, and nitrate. The formation of these complexes will increase the concentrations of total dissolved thorium in soil- and groundwaters. Recent studies of carbonate complexation of dissolved thorium indicate that the speciation of dissolved thorium may be dominated by mixed thorium

carbonate and hydroxyl-carbonate complexes, such as  $\text{Th}(\text{OH})_3\text{CO}_3^-$ , at pH values greater than 7.5. Species distributions calculated using the stability constants for thorium citrate, oxalate, and ethylenediamine complexes indicate that thorium organic complexes likely predominate over inorganic complexes in organic-rich waters and soils. This would have an important effect on the solubility and adsorption of thorium in such waters.

Thorium-containing minerals, such as thorite, thorianite, monazite, and zircon, do not dissolve readily in low-temperature surface- and groundwaters. Because these minerals form at temperature and pressure conditions associated with igneous and metamorphic rocks, it is unlikely that the concentration of thorium in soil/water environments is controlled by the solubility of any of these minerals. The rate at which thorium is released to the environment may however be controlled by the rates of dissolution of 1 or more of these phases. The maximum possible concentration of thorium dissolved in low-temperature aqueous systems can however be predicted with the solubility of hydrous thorium oxide, because the solubility of this compound will result in higher concentrations of dissolved thorium than will likely occur from the kinetically-hindered dissolution of resistant primary thorium minerals. Moreover, hydrous thorium oxide solid is known to precipitate in laboratory experiments (*i.e.*, short time periods) conducted at low temperature, oversaturated conditions.

The concentrations of dissolved thorium in surface and groundwaters may also be controlled to low values by adsorption processes. Humic substances are considered particularly important in the adsorption of thorium. The available partition coefficient,  $K_d$ , data indicates significant retention of thorium by most soil types.

### 5.9.2 General Geochemistry

Twelve isotopes of thorium are known. Their atomic masses range from 223 to 234, and all are unstable (or radioactive) (Weast and Astle, 1980). Of these, 6 thorium isotopes exist in nature. These include:

- $^{238}\text{U}$  decay series:  $^{234}\text{Th}$  [ $t_{1/2}$  (half life) = 24.1 d] and  $^{230}\text{Th}$  ( $t_{1/2} = 8.0 \times 10^4$  y)
- $^{232}\text{Th}$  decay series:  $^{232}\text{Th}$  ( $t_{1/2} = 1.41 \times 10^{10}$  y) and  $^{228}\text{Th}$  ( $t_{1/2} = 1.913$  y)
- $^{235}\text{U}$  decay series:  $^{231}\text{Th}$  ( $t_{1/2} = 25.5$  h) and  $^{227}\text{Th}$  ( $t_{1/2} = 18.5$  d).

Natural thorium consists of essentially 1 isotope,  $^{232}\text{Th}$ , with trace quantities of the other isotopes. Thorium is fertile nuclear material in that the principal isotope  $^{232}\text{Th}$  can be converted by capture of a thermal neutron and 2 beta decays to fissionable  $^{233}\text{U}$  which does not exist in nature. The application of thorium as a reactor fuel in the  $\text{ThO}_2$  ceramic form is described in detail by Belle and Berman (1984).

Thorium occurs only in the +4 oxidation state in nature. The  $\text{Th}^{4+}$  ion is the largest tetravalent cation known with a radius of approximately 1.0 Å. Although the  $\text{Th}^{4+}$  ion is more resistant to hydrolysis than other tetravalent ions, it forms a variety of hydroxyl species at pH values above 3 (Baes and Mesmer,

1976; Cotton and Wilkinson, 1980). The thorium content in natural water is very low. The concentration range in natural fresh water rarely exceeds 1 micro g/l (0.1 pCi/l  $^{232}\text{Th}$ ), although mg/l concentrations of  $^{232}\text{Th}$  have been detected in high-acid groundwaters beneath uranium tailings sites (Langmuir and Herman, 1980).

Although the normal ranges of thorium concentrations in igneous, metamorphic, and sedimentary rocks are less than 50 ppm, thorium concentrations can be as high as 30 and 300 ppm, respectively, in oceanic sand/clays and marine manganese nodules (Gascoyne, 1982). These anomalously high concentrations of thorium have been explained by the tendency of thorium to strongly adsorb on clay and oxyhydroxide phases (Langmuir and Herman, 1980).

The mineralogy of thorium-containing minerals is described by Frondel (1958). Most thorium-containing minerals are considered fairly insoluble and resistant to erosion. There are few minerals in which thorium is an essential structural constituent. Important thorium minerals include thorite  $[(\text{Th}, \text{U}, \text{Ce}, \text{Fe}, \text{etc.})\text{SiO}_4]$  and thorianite (crystalline  $\text{ThO}_2$ ). Thorite is found in pegmatites, gneisses, granites, and hydrothermal deposits. Thorianite is chiefly found in pegmatitic rocks, but is best known as a detrital mineral.<sup>1</sup> Thorium also occurs, however, as variable, trace concentrations in solid solution in many rare-earth, zirconium, and uranium minerals. The 2 most important minerals of this type include monazite  $[(\text{Ce}, \text{La}, \text{Th})\text{PO}_4]$  and zircon ( $\text{ZrSiO}_4$ ). Monazite and zircon are widely disseminated as accessory minerals in igneous and metamorphic rocks. They also occur in commercial quantities in detrital sands derived from regions of these rocks due to their resistance to erosion (Deer *et al.*, 1967; Frondel, 1958). Concentrations of thorium can be several weight percent in these deposits.

Because of their long half lives,  $^{228}\text{Th}$  ( $t_{1/2} = 1.913 \text{ y}$ ),  $^{230}\text{Th}$  ( $t_{1/2} = 8.0 \times 10^4 \text{ y}$ ), and  $^{232}\text{Th}$  ( $t_{1/2} = 1.41 \times 10^{10} \text{ y}$ ), which are all alpha-particle emitters, pose long-term health risks and are therefore environmentally important. Contamination includes thorium-containing soils and thorium dissolved in surface- and groundwaters. Of the contaminated sites considered in EPA/DOE/NRC (1993), radioactive contamination of soil, surface water, and/or groundwater by  $^{228}\text{Th}$ ,  $^{230}\text{Th}$ , and/or  $^{232}\text{Th}$  has been identified at 21 of the 45 Superfund National Priorities List (NPL) sites and 23 of the 38 NRC Site Decommissioning Management Plan (SDMP) sites. Some of the contamination resulted from the separation and processing of uranium and from the use of monazite and zircon sands as source materials for metallurgical processes.

### 5.9.3 Aqueous Speciation

Thorium occurs only in the +4 oxidation state in natural soil/water environments. Dissolved thorium forms a variety of hydrolytic species, and, as a small, highly charged ion, undergoes extensive chemical

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<sup>1</sup> A detrital mineral is defined as “any mineral grain resulting from mechanical disintegration of parent rock” (Bates and Jackson, 1980).

interaction with water and most anions. The available thermodynamic data for thorium-containing aqueous species and solids have been compiled and critically reviewed by Langmuir and Herman (1980) for an analysis of the mobility of thorium in low-temperature, natural waters.

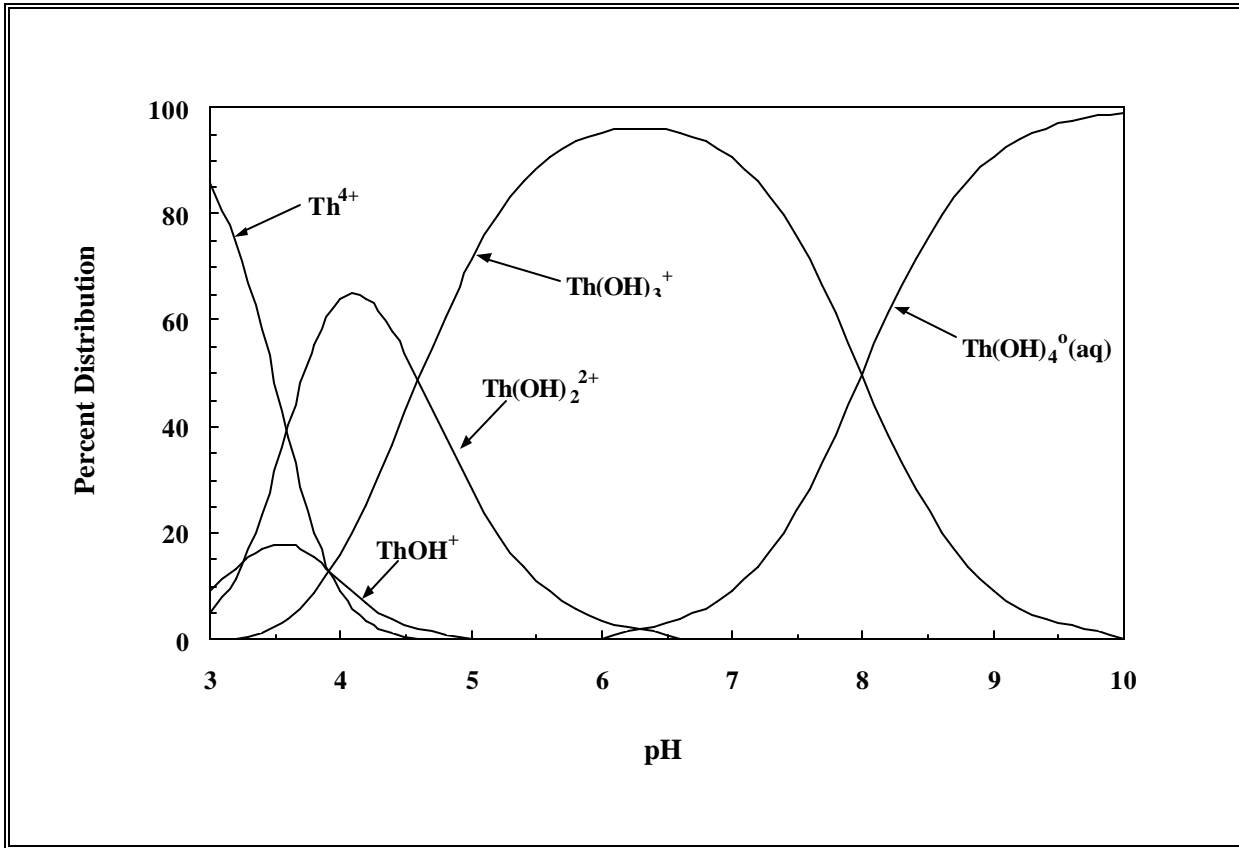
Thorium undergoes hydrolysis in aqueous solutions at pH values above 3. The distribution of thorium hydrolytic species, shown in Figure 5.4, was calculated as a function of pH using the MINTEQA2 code and the thermodynamic data tabulated in Langmuir and Herman (1980). The aqueous species included in the speciation calculations are listed in Table 5.14. The species distribution in Figure 5.4 was determined for a concentration of 1 micro g/l total dissolved thorium for a water free of any complexing ligands other than hydroxide ions. The chosen thorium concentration is based on Hem (1985, p. 150) who gives 0.01 to 1 micro g/l as the range expected for thorium concentrations in fresh waters. The calculated species distribution shows that the uncomplexed ion  $\text{Th}^{4+}$  is the dominant ion at pH values less than ~3.5. At pH values greater than 3.5, the hydrolysis of thorium is dominated, in order of increasing pH, by the aqueous species  $\text{Th}(\text{OH})_2^{2+}$ ,  $\text{Th}(\text{OH})_3^+$ , and  $\text{Th}(\text{OH})_4^{\text{aq}}$ . The latter 2 hydrolytic complexes have the widest range of stability with pH.

The large effective charge of the  $\text{Th}^{4+}$  ion can induce hydrolysis to the point that polynuclear complexes may form (Baes and Mesmer, 1976). Present knowledge of the formation of polynuclear hydrolyzed species is poor because there is no unambiguous analytical technique to determine these species. However, polynuclear species are believed to play a role in mobility of thorium in soil/water systems. Langmuir and Herman (1980) list estimated thermodynamic values for the thorium polynuclear hydrolyzed species  $\text{Th}_2(\text{OH})_2^{6+}$ ,  $\text{Th}_4(\text{OH})_8^{8+}$ , and  $\text{Th}_6(\text{OH})_{15}^{9+}$  based on the review of Baes and Mesmer (1976).

**Table 5.14.** Thorium aqueous species included in the speciation calculations.

| Aqueous Species   |
|---|
| $\text{Th}^{4+}$ , $\text{ThOH}^{3+}$ , $\text{Th}(\text{OH})_2^{2+}$ , $\text{Th}(\text{OH})_3^+$ , $\text{Th}(\text{OH})_4^0(\text{aq})$ ,<br>$\text{Th}_2(\text{OH})_2^{6+}$ , $\text{Th}_4(\text{OH})_8^{8+}$ , $\text{Th}_6(\text{OH})_{15}^{9+}$<br><br>$\text{Th}(\text{OH})_3\text{CO}_3^-$ and $\text{Th}(\text{CO}_3)_5^{6-}$<br><br>$\text{ThF}^{3+}$ , $\text{ThF}_2^{2+}$ , $\text{ThF}_3^+$ , $\text{ThF}_4^0(\text{aq})$<br><br>$\text{ThCl}^{3+}$ , $\text{ThCl}_2^{2+}$ , $\text{ThCl}_3^+$ , $\text{ThCl}_4^0(\text{aq})$<br><br>$\text{ThSO}_4^{2+}$ , $\text{Th}(\text{SO}_4)_2^0(\text{aq})$ , $\text{Th}(\text{SO}_4)_3^{2-}$ , $\text{Th}(\text{SO}_4)_4^{4-}$<br><br>$\text{ThH}_3\text{PO}_4^{4+}$ , $\text{ThH}_2\text{PO}_4^{3+}$ , $\text{Th}(\text{H}_2\text{PO}_4)_2^{2+}$ ,<br>$\text{Th}(\text{HPO}_4)_2^0(\text{aq})$ , $\text{Th}(\text{HPO}_4)_3^{2-}$ |

In addition to hydrolytic complexes, thorium can also form various aqueous complexes with inorganic anions such as dissolved fluoride, phosphate, chloride, and nitrate. Studies (*e.g.*, LaFamme and Murray, 1987) completed since the review by Langmuir and Herman (1980) indicate the presence of dissolved thorium carbonate complexes and their importance to the solution chemistry of thorium. Due to the lack of available data, no thorium carbonate species were listed by Langmuir and Herman (1980). Östhols *et al.* (1994) have recently published thermodynamic constants for the thorium carbonate complexes  $\text{Th}(\text{OH})_3\text{CO}_3^-$  and  $\text{Th}(\text{CO}_3)_5^{6-}$  that are based on their solubility studies of microcrystalline  $\text{ThO}_2$  at different partial pressures of  $\text{CO}_2$  in aqueous media.



**Figure 5.4.** Calculated distribution of thorium hydrolytic species as a function of pH. [The species distribution is based on a concentration of 1 micro g/l total dissolved thorium in pure water (*i.e.*, absence of complexing ligands other than OH) and thermodynamic data from Langmuir and Herman (1980).]

The distribution of thorium aqueous species (Figure 5.5) was also calculated as a function of pH using the MINTEQA2 for a concentration of 1 micro g/l total dissolved thorium and the water composition in Table 5.1. The thermodynamic data were principally from Langmuir and Herman (1980). The thermodynamic constants for the aqueous species  $\text{Th}(\text{OH})_3\text{CO}_3^-$  and  $\text{Th}(\text{CO}_3)_5^{6-}$  from Östholts *et al.* (1994) were also included in these speciation calculations. Below pH 5, dissolved thorium is dominated by thorium fluoride complexes. Between pH 5 and 7, dissolved thorium is predicted to be dominated by thorium phosphate complexes. Although phosphate complexation is expected to have a role in the mobility of thorium in this range of pH values, the adequacy of the thermodynamic constants tabulated for thorium phosphate complexes in Langmuir and Herman (1980) are suspect, and may over predict the stability of these complexes. At pH values greater than 7.5, more than 95 percent of the dissolved thorium is predicted to be present as  $\text{Th}(\text{OH})_3\text{CO}_3^-$ . The species distribution illustrated in

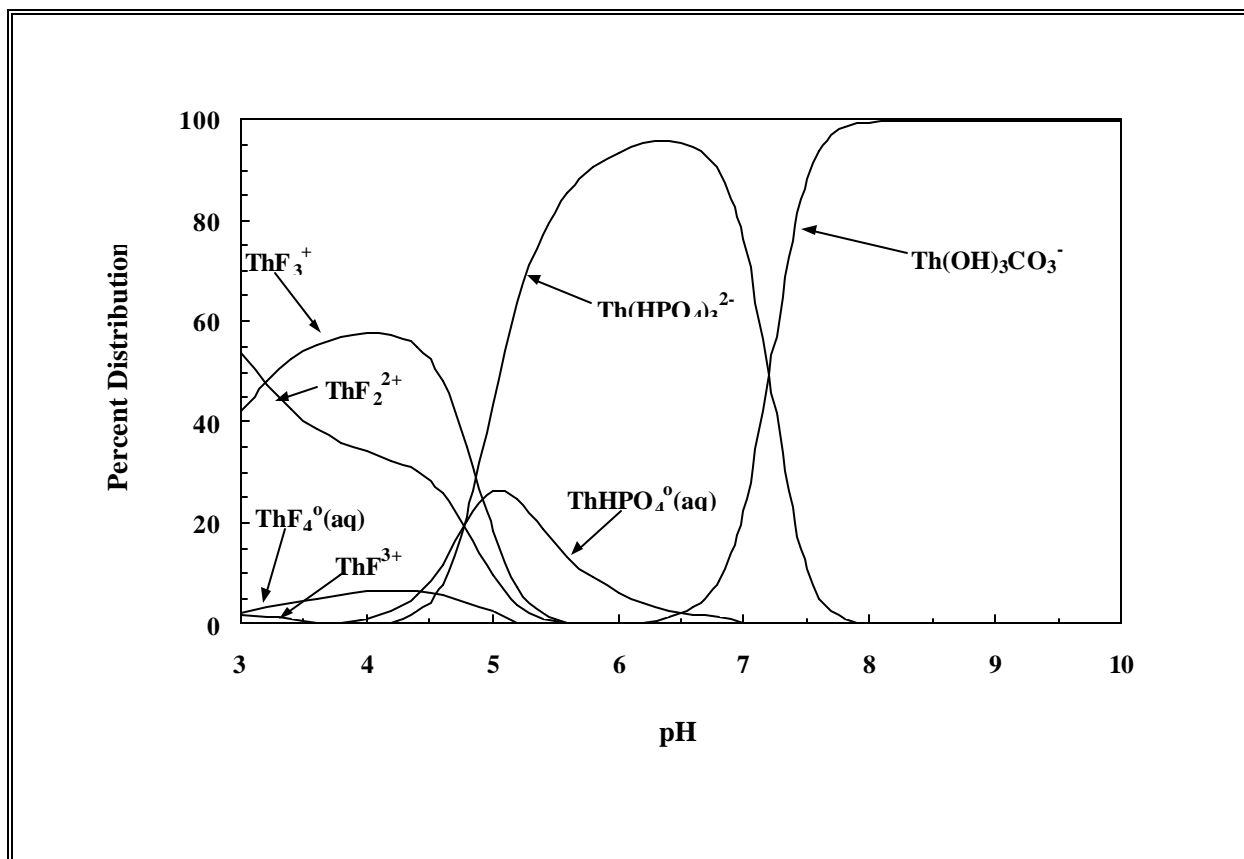
Figure 5.5 changes slightly in the pH range from 5 to 7 if the concentration of total dissolved thorium is increased from 1 to 1,000 micro g/l. At the higher concentration of dissolved thorium, the stability of  $\text{Th}(\text{OH})_3\text{CO}_3^-$  extends to a pH of approximately 5, the hydrolytic species  $\text{Th}(\text{OH})_3^-$  becomes an important species (about 30 percent of the dissolved thorium), and the thorium phosphate species are no longer dominant.

Thorium organic complexes likely have an important effect on the mobility of thorium in soil/water systems. Langmuir and Herman (1980) used citrate ( $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ), oxalate ( $\text{C}_2\text{O}_4^{2-}$ ), and ethylenediamine tetra-acetic acid (EDTA) ( $\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2^{4-}$ ) to show the possible role of organic complexes in the mobility of thorium in natural waters. Based on the stability constants available for thorium citrate, oxalate, and ethylenediamine complexes, calculations by Langmuir and Herman (1980) indicate that thorium organic complexes likely predominate over inorganic complexes in organic-rich waters and soils. For the concentrations considered by Langmuir and Herman (1980), the  $\text{ThEDTA}^-(\text{aq})$  complex dominates all other thorium aqueous species over the pH range from 2 to 8. This would in turn have an important effect on the solubility and adsorption of thorium in such waters.

#### ***5.9.4 Dissolution/Precipitation/Coprecipitation***

The main thorium-containing minerals, thorite  $[(\text{Th}, \text{U}, \text{Ce}, \text{Fe}, \text{etc.})\text{SiO}_4]$ , thorianite (crystalline  $\text{ThO}_2$ ), monazite  $[(\text{Ce}, \text{La}, \text{Th})\text{PO}_4]$  and zircon ( $\text{ZrSiO}_4$ ), are resistant to chemical weathering and do not dissolve readily at low-temperature in surface and groundwaters. Because these minerals form at temperature and pressure conditions associated with igneous and metamorphic rocks, it is unlikely that the thermodynamic *equilibrium* solubilities (where the rate of precipitation equals the rate of dissolution) of these minerals will control the concentration of dissolved thorium in low-temperature soil/water environments. The rate at which thorium is released to the environment, as might be needed in a source-term component of a performance assessment model, may however be controlled by the kinetic rates of aqueous dissolution (*i.e.*, *non-equilibrium* conditions) of 1 or more of these phases.





**Figure 5.5.** Calculated distribution of thorium aqueous species as a function of pH for the water composition in Table 5.1. [The species distribution is based on a concentration of 1 micro g/l total dissolved thorium and thermodynamic data from Langmuir and Herman (1980) and Östhols *et al.* (1994, for  $\text{Th}(\text{OH})_3\text{CO}_3^-$  and  $\text{Th}(\text{CO}_3)_5^{6-}$ ). The thermodynamic database used for these speciation calculations did not include the constants for thorium humic acid complexes.]

The maximum concentration of dissolved thorium that may occur in a low-temperature aqueous system can be predicted with the solubility of hydrous thorium oxide. This solid is known to precipitate in laboratory experiments conducted at low temperature, oversaturated conditions over several weeks. If this solid precipitates in a natural environment, it will likely alter with time to a more crystalline solid that has a lower solubility. The solubility of hydrous thorium oxide has been studied experimentally by Rai and coworkers (Felmy *et al.*, 1991; Rai *et al.*, 1995; Ryan and Rai, 1987). In 0.1 M  $\text{NaClO}_4$  solutions, the measured solubility of hydrous thorium oxide ranges from about  $10^{-8.5}$  mol/l (0.0007 mg/l)

to less than  $10^{-9}$  mol/l (0.0002 mg/l) in the pH range from 5 to 10 (Ryan and Rai, 1987). The concentration of dissolved thorium increases to approximately  $10^{-2.6}$  mol/l (600 mg/l) as pH decreases from 5.0 to 3.2.

Felmy *et al.* (1991) determined that the solubility of hydrous thorium oxide increases with increasing ionic strength. At pH values above 7 in 3.0 M NaCl solutions, the solubility of hydrous thorium oxide increased by approximately 2 to 3 orders of magnitude compared to that determined in 0.1 M NaClO<sub>4</sub> solutions. Moreover, the pH at which hydrous thorium oxide exhibits rapid increases in solubility with decreasing pH changes from pH 5 in 0.1 M NaClO<sub>4</sub> to approximately pH 7 in 3.0 M NaCl. In studies conducted at high hydroxide and carbonate concentrations, Rai *et al.* (1995) determined that the solubility of hydrous thorium oxide increases dramatically in high carbonate solutions and decreases with increases in hydroxide concentration at fixed carbonate concentrations. This supports the assertion that soluble thorium-carbonate complexes likely dominate the aqueous speciation of thorium dissolved in natural waters having basic pH values.

#### 5.9.5 Adsorption/Desorption

Thorium concentrations in surface- and groundwaters may also be controlled to very low levels ( $\leq$  few micro g/l) by adsorption processes. Humic substances are considered particularly important in the adsorption of thorium (Gascoyne, 1982). Thibault *et al.* (1990) conducted a critical compilation and review of published  $K_d$  data by soil type needed to model radionuclide migration from a nuclear waste geological disposal vault to the biosphere. Thibault *et al.* list  $K_d$  values for thorium that range from 207 to 13,000,000 ml/g. The range of thorium  $K_d$  values listed for organic soil was 1,579 to  $1.3 \times 10^7$  ml/g. Based on our experience, the very high  $K_d$  values reported for thorium should be viewed with caution. The studies resulting in these values should be examined to determine if the initial concentrations of thorium used for these  $K_d$  measurements were too great and precipitation of a thorium solid (*e.g.*, hydrous thorium oxide) occurred during the equilibration of the thorium-spiked soil/water mixtures. As noted in the letter report for Subtask 1B, precipitation of solids containing the contaminant of interest results in  $K_d$  values that are erroneously too high.

The adsorption of thorium on pure metal-oxide phases has also been studied experimentally in conjunction with surface complexation models.<sup>1</sup> Östhols (1995) studied the adsorption of thorium on amorphous colloidal particles of silica (SiO<sub>2</sub>). Their results indicate that the adsorption of thorium on silica will only be important in the pH range from 3 to 6. In neutral and alkaline pH values, silica surface sites are not expected to be efficient adsorbents for thorium.

Iron and manganese oxides are expected to be more important adsorbents of thorium than silica. Hunter *et al.* (1988) studied the adsorption of thorium on goethite ( $\alpha$ -FeOOH) and nsutite ( $\gamma$ -MnO<sub>2</sub>)

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<sup>1</sup> Surface complexation models are discussed in Volume I of this report.

in marine electrolyte solutions. Their experiments indicate that adsorption of thorium increases from approximately 0 percent at pH 2.5-3.5 to 90-100 percent at pH 5-6.5. The adsorption of thorium decreased with the addition of sulfate as a result of the formation of competitive aqueous complexes with dissolved thorium. The addition of organic ligands EDTA and trans-1,2-diaminocyclohexane tetra-acetic acid (CDTA) shifted the adsorption edges for  $\gamma$ -MnO<sub>2</sub> to higher pH values by more than 5-6 pH units, such that 100 percent adsorption of thorium was not observed until pH 12. LaFlamme and Murray (1987) experimentally studied the effects of pH, ionic strength and carbonate alkalinity on the adsorption of thorium by goethite. The adsorption edge (*i.e.*, range in pH where metal adsorption goes from 0 percent to approximately 90-100 percent) was measured to be in the pH range from 2 to 5. For conditions considered in their study, ionic strength was found to have no effect on the adsorption of thorium on goethite. LaFlamme and Murray did however observe a strong influence of carbonate alkalinity on thorium adsorption. In their experiments at pH 9.0±0.6, they observed a decrease of thorium adsorption with the addition of 100 meq/l carbonate alkalinity, and no measurable adsorption of thorium at carbonate alkalinity greater than 300 meq/l. At the low particle concentrations used in their experiments, LaFlamme and Murray attributed this reduction to the competition for surface sites by CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> and the formation of soluble thorium-carbonate complexes with a net negative charge.

### 5.9.6 Partition Coefficient, $K_d$ , Values

#### 5.9.6.1 General Availability of $K_d$ Data

Two generalized, simplifying assumptions were established for the selection of thorium  $K_d$  values for the look-up table. These assumptions were based on the findings of the literature review conducted on the geochemical processes affecting thorium sorption. The assumptions are as follows:

- Thorium precipitates at concentrations greater than 10<sup>-9</sup> M. This concentration is based on the solubility of Th(OH)<sub>4</sub> at pH 5.5. Although (co)precipitation is usually quantified with the solubility construct, a very large  $K_d$  value will be used in the look-up table to approximate thorium behavior in systems with high thorium concentrations.
- Thorium adsorption occurs at concentrations less than 10<sup>-9</sup> M. The extent of thorium adsorption can be estimated by soil pH.

These assumptions appear to be reasonable for a wide range of environmental conditions. However, these simplifying assumptions are clearly compromised in systems containing high alkaline (LaFlamme and Murray, 1987), carbonate (LaFlamme and Murray, 1987), or sulfate (Hunter *et al.*, 1988) concentrations, and high or low pH values (pH: 3 < x > 8: Hunter *et al.*, 1988; LaFlamme and Murray 1987; Landa *et al.*, 1995). These assumptions will be discussed in more detail in the following sections.

Based on the assumptions and limitations described above, thorium  $K_d$  values and some important ancillary parameters that influence sorption were collected from the literature and tabulated (Appendix I). Data included in this table, were from studies that reported  $K_d$  values (not percent adsorbed or Freundlich or Langmuir constants) and were conducted in systems consisting of:

- Low ionic strength ( $< 0.1$  M)
- pH values between 4 and 10.5
- Dissolved thorium concentrations less than  $10^{-9}$  M
- Low humic material concentrations ( $< 5$  mg/l)
- No organic chelates (*e.g.*, EDTA)

These aqueous chemistry constraints were selected to limit the thorium  $K_d$  values evaluated to those that would be expected to exist in a far-field. The ancillary parameters included in these tables were clay content, calcite concentration, pH, and CEC. Attempts were also made to include in the data set the concentration of organic carbon and aluminum/iron oxides in the solid phase. However, these latter ancillary parameters, which were identified above, were rarely included in the reports evaluated to compile the data set. The data set included 17 thorium  $K_d$  values for soils and pure phase minerals.

#### 5.9.6.2 Look-Up Tables

Linear regression analyses were conducted with data collected from the literature (described in Appendix I). These analyses were used as guidance for selecting appropriate  $K_d$  values for the look-up table. The  $K_d$  values used in the look-up tables could not be based entirely on statistical consideration because the statistical analysis results were occasionally nonsensical. For example, the data showed a negative correlation between clay content and thorium  $K_d$  values. This trend contradicts well established principles of surface chemistry. Instead, the statistical analysis was used to provide guidance as to the approximate range of values to use and to identify meaningful trends between the thorium  $K_d$  values and the solid phase parameters. Thus, the  $K_d$  values included in the look-up table were in part selected based on professional judgment. Again, only low-ionic strength solutions, similar to that expected in far-field groundwaters, were considered in these analyses.

The look-up table for thorium  $K_d$  values was based on plume thorium concentrations and pH. These 2 parameters have an interrelated effect on thorium  $K_d$  values. The maximum concentration of dissolved thorium may be controlled by the solubility of hydrous thorium oxides (Felmy *et al.*, 1991; Rai *et al.*, 1995; Ryan and Rai, 1987). The dissolution of hydrous thorium oxides may in turn vary with pH. Ryan and Rai (1987) reported that the solubility of hydrous thorium oxide is  $\sim 10^{-8.5}$  to  $\sim 10^{-9}$  in the pH range of 5 to 10. The concentration of dissolved thorium increases to  $\sim 10^{-2.6}$  M (600 mg/L) as pH decreases from 5.0 to 3.2. Thus, 2 categories based on thorium solubility were included in the look-up table, pH 3 to 5, and pH 5 to 10. Although precipitation is typically quantified by the solubility construct, a very large  $K_d$  value was used in the look-up table to describe high thorium concentrations

(Table 5.15). See Appendix I for a detailed account of the process used to select the  $K_d$  values in Table 5.15.

#### 5.9.6.2.1 Limits of $K_d$ Values with Respect to Organic Matter and Aluminum/Iron-Oxide Concentrations

Of the 17 entries in the thorium  $K_d$  data set (Appendix I), none of them had accompanying organic matter or aluminum- and iron-oxide mineral concentration data. It was anticipated that the presence of organic matter would decrease thorium  $K_d$  values by forming thorium-organic matter complexes. These complexes would be less prone to adsorb to surface than the uncomplexed thorium species. Conversely, it was anticipated that the presence of aluminum- and/or iron-oxides would increase thorium  $K_d$  values by increasing the number of adsorption (surface complexation) sites.

#### 5.9.6.2.2 Limits of $K_d$ Values with Respect to Dissolved Carbonate Concentrations

Of the 17 entries in the thorium  $K_d$  data set (Appendix I), none of them had accompanying carbonate concentration data. However, 5 entries had calcite ( $\text{CaCO}_3$ ) mineral concentrations. It was anticipated that calcite concentrations could be used as an indirect measure, albeit poor measure, of the amount of dissolved carbonate in the aqueous phase. Calcite concentrations had a correlation coefficient ( $r$ ) with thorium  $K_d$  value of 0.76 (Appendix I). Although this is a relatively high correlation value, it is not significant at the 5 percent level of probability due to the small number of observations (5 observations). Furthermore, it was anticipated that the presence of dissolved carbonate would decrease thorium  $K_d$  values due to formation of the weaker forming carbonate-thorium complexes.

**Table 5.15.** Look-up table for thorium  $K_d$  values (ml/g) based on pH and dissolved thorium concentrations. [Tabulated values pertain to systems consisting of low ionic strength ( $< 0.1$  M), low humic material concentrations ( $< 5$  mg/l), no organic chelates (*e.g.*, EDTA), and oxidizing conditions.]

| $K_d$ (ml/g) | pH                |              |                   |            |                   |            |
|--------------|-------------------|--------------|-------------------|------------|-------------------|------------|
|              | 3 - 5             |              | 5 - 8             |            | 8 - 10            |            |
|              | Dissolved Th, $M$ |              | Dissolved Th, $M$ |            | Dissolved Th, $M$ |            |
|              | $<10^{-2.6}$      | $>10^{-2.6}$ | $<10^{-9}$        | $>10^{-9}$ | $<10^{-9}$        | $>10^{-9}$ |
| Minimum      | 62                | 300,000      | 1,700             | 300,000    | 20                | 300,000    |
| Maximum      | 6,200             | 300,000      | 170,000           | 300,000    | 2,000             | 300,000    |